# EVALUATION OF NOVEL SOIL AMENDMENTS IN REDUCING HEAVY METAL AND EMERGING ORGANIC CONTAMINANT POLLUTION FROM WASTEWATER IRRIGATION IN SOIL-PLANT SYSTEMS

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# Abstract

The world's rapidly growing food needs have led to a greater demand for freshwater for irrigated agricultural production. In many developing countries, farmers facing water scarcity resort to partially-treated or untreated wastewater for irrigation; however, these countries' wastewater treatment plants seldom have the technology to efficiently remove conventional [e.g., heavy metals] and emerging contaminants [e.g., pharmaceuticals and personal care products (PPCPs)], from wastewater. Given the risk they pose to human, animal and aquatic life, and the critical need to develop cost-effective, user-friendly techniques to lower the risk posed by these contaminants, an understanding of how they accumulate in soil, crops and in ground- or surface waters, achieved through the monitoring of their fate in the environment, is key to successfully mitigating their adverse effects. Biochar (BC) and compost (CP) soil amendments can immobilize several heavy metals and organic contaminants in soil and thereby reduce their uptake by plants. While the presence of nanoparticles (NPs) have shown promise in reducing the uptake of contaminants in plants; however, given the paucity of soil-plant system studies investigating the effects of NPs delivered to the soil via irrigation, the potential effects of NPs on soil-crop systems are poorly understood.

Accordingly, a two-year field lysimeter study (2017-2018), laid out in a thrice-replicated randomized design was implemented to investigate: (i) the effects of soil amendments of barley straw biochar and green table waste compost, applied alone or in combination, and (ii) the effects of TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub>-NPs) delivered in wastewater, on the transport within the soil of wastewater-irrigation-delivered coexisting inorganic and organic contaminants, and their uptake by a crop (potatoes). The biochar/compost soil amendment treatments were: (*i*) non-amended soil (*ii*) 1% BC alone; (*iii*) 3% BC alone; (*iv*) 7.5% CP alone; (*v*) 1% BC and 7.5% CP; (*vi*) 3%

BC and 7.5% CP. Treatments in the irrigation-water-delivered TiO<sub>2</sub>-NPs experiment, included: (*i*) synthetic wastewater (WW) (*ii*) freshwater (FW), and (*iii*) wastewater bearing TiO<sub>2</sub>-NPs. Treatments impacts on soil properties, along with contaminant mobility and uptake by potato plants were monitored. Alone or mixed with biochar, compost provided a more effective reduction in the uptake of Cd, Cu and Zn into plants and in retaining heavy metals in the topsoil, than did other treatments. Similar effects for these metals were observed under the TiO<sub>2</sub>-NPs (*vs.* WW control). A biochar (*vs.* compost) amendment showed a greater ( $p \le 0.05$ ) effect on mobility of PPCPs. Crop Cr, Fe, and Pb uptake remained unaffected by any treatment.

The effects of soil biochar/compost amendment on potato growth and yield assessed at maturity varied over the two seasons: (*i*) potato yield was significantly lower ( $p \le 0.05$ ) after the warmer 2018 growing season than in 2017, (*ii*) in 2018, unlike 2017, the 3% BC treatment provided a greater yield than other treatments, likely attributable to biochar's greater ( $p \le 0.05$ ) stability in soil into a second season, (*iii*) soil amendments had no significant effect on plant health parameters. Overall, biochar and compost (alone and mixed) reduced plant uptake of certain heavy metals and organic contaminants' mobility by improving soil properties, thereby facilitating immobilization. This suggests that soil amendments and the presence of NPs in wastewater can contribute to the safe use of wastewater for irrigation.

#### Résumé

La rapide croissance des besoins alimentaires mondiaux engendre une plus grande demande en eau douce afin d'approvisionner une production agricole irriguée. es Les producteurs agricoles de plusieurs pays en voie de développement, faisant face à une pénurie d'eau ont recours à des eaux usées partiellement- ou non-traités pour irriguer. Cependant, ces pays ont rarement accès à des technologies leur permettant d'éliminer les contaminants conventionnels (c.à.d., métaux lourds) et émergents [c.à.d., produits pharmaceutiques et de soins personnels (PPSPs)] des eaux usées. Vu le risque que ceux-ci posent à la vie humaine, animale et aquatique, et la nécessité absolue de développer des méthodes rentables et pratiques permettant de réduire le risque que posent ces contaminants, une solide compréhension de la manière qu'ils s'accumulent dans le sol, dans les cultures et dans les eaux de surface et souterraines, fondé sur le suivi de leur devenir dans l'environnement, est essentielle à l'atténuation de leurs effets néfastes. L'amendement du sol avec du charbon à usage agricole (biochar, BC) ou avec du compost (CP), permettrait d'immobiliser plusieurs métaux lourds et contaminants organiques présents dans le sol, et ainsi réduire leur assimilation par les cultures. Quoique la présence de nanoparticules (NPs) s'est avérée prometteur quant à la réduction de l'assimilation de contaminants par les plantes, il demeure que le peu d'études sur les systèmes sol-plante s'adressant aux effets de NPs livrées au sol par voie d'irrigation, laissent les effets potentiels des NPs sur les systèmes sol-culture largement inconnus.

Par conséquence, une étude en lysimètres sur deux ans (2017-2018), disposée en bloc aléatoire complet avec trois répétitions, fut entreprise afin d'enquêter sur : (i) les effets de l'amendement du sol avec du biochar à base de paille d'orge et de composte de déchets végétaux de cuisine, seuls ou en combinaison, et (ii) l'effet de nanoparticules de TiO<sub>2</sub> livrées par voie de l'eau usée servant à l'irrigation, sur le transport dans le sol de contaminants organiques et inorganiques co-existant livrés dans ces mêmes eaux usées, et l'assimilation de ceux-ci par la culture (pomme de terre). Les traitements d'amendements du sol avec biochar/compost inclurent : (*i*) aucun amendement; (*ii*) BC uniquement, 1%; (*iii*) BC uniquement, 3%; (*iv*) CP uniquement, 7.5%; (*v*) BC 1% avec CP 7.5%, et (*vi*) BC 3% avec CP 7.5%. Les traitements pour l'étude avec les NP de TiO<sub>2</sub> livrés dans l'eau usée servant à l'irrigation inclurent: (*i*) eau usée synthétique, (*iii*) eau douce, et eau usée contenant des NP de TiO<sub>2</sub>. L'impact des traitements sur les propriétés du sol, la mobilité des contaminants et leur assimilation par les plants de pomme de terre furent suivis. Seul et en combinaison avec du biochar, le compost présenta à la fois un meilleur contrôle de l'assimilation du Cd, Cu, et Zn par les plantes, et leur plus grande rétention dans le sol, par rapport aux autres traitements. Par rapport à l'étalon d'eau usée, des effets semblables vis à vis ces métaux furent notés pour le traitement avec NP de TiO<sub>2</sub>. Un amendement du sol avec du biochar (*vs.* compost), eut un plus grand effet ( $p \le 0.05$ ) de réduction sur la mobilité des PPSPs. L'assimilation du Cr, Fe et Pb par les plantes ne fut pas influencé par quelque traitement que ce soit.

Les effets des amendements du sol avec biochar et/ou compost sur la croissance des plants de pommes de terre, et leur rendement à la maturité furent différentes d'année en année : (i) le rendement en pommes de terre fut significativement moins élevé ( $p \le 0.05$ ) suivant la saison plus chaude de 2018 (vs. 2017), (*ii*) en 2018, mais non en 2017, the traitement de BC à 3% offra un rendement plus élevé que tout autre traitement, probablement parce que le biochar dans le sol demeura plus stable ( $p \le 0.05$ ) lors de la seconde saison, (*iii*) les amendements n'eurent aucun effet sur la santé des plantes. En somme, les amendements de biochar et le compost (seuls ou en combinaison), en améliorant les propriétés du sol et facilitant ainsi l'immobilisation de contaminants, ont réduit l'assimilation de certains métaux par la culture lourds, ainsi que la mobilité de contaminants organiques dans le sol. On peut en conclure que

des amendements au sol et la présence de NPs dans les eaux usées servant à l'irrigation peuvent contribuer à une utilisation en toute sécurité d'eaux usées à fin d'irrigation.

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# Dedication

To my parents (Almabrouk & Nariman) and my lovely children (Almabrouk & Nariman) for their love and patience and my newborn twins (Layan & Lujain).

## **Thesis Format and Contribution of Authors**

Following the Guidelines Concerning Thesis Preparation issued by McGill University Graduate and Postdoctoral Studies. this thesis is written in manuscript format by the candidate. The thesis consists of four manuscripts with chapters whereas the manuscripts have been submitted for publication to peer reviewed journals and/or are under preparation. In all manuscripts, the candidate is the senior author and was responsible for experimental design and conducting all experiments, data collection, analysis, interpretation of data, and Writing - original draft. Prof. Shiv Prasher as thesis supervisor, and Prof. Stéphane Bayen as thesis co-supervisor, were actively involved at every stage of the study and provided invaluable scientific and technical advice, co-authored all the manuscripts.

- Prof. Shiv Prasher Department of Bioresource Engineering McGill University, Funding acquisition, Conceptualization, Project administration, Methodology, Resources, Supervision, Writing review and editing.
- Prof. Stéphane Bayen Department of Food science and Agricultural Chemistry McGill University, Supervision, Data curation, Validation, Writing - review and editing.
- Prof. Kevin J. Wilkinson Department of Chemistry University of Montreal, co-authors for nanoparticles chapters 6, he was involved in the nanoparticle's analysis and Writing review and editing.
- Prof. Saji George Department of Food science and Agricultural Chemistry McGill University, co-authors for nanoparticle chapter 6, he was involved in the Methodology, Writing review and editing.
- Dr. Lan Liu Department of Food science and Agricultural Chemistry McGill University, coauthors for chapter 5, she was involved in the Data Curation, Methodology, and Formal analysis.

- Ms. Emma C. Anderson Department of Bioresource Engineering McGill University, co-author of chapters 3 and 6, she was involved in Methodology, Writing review and editing.
- Dr. Eman ElSayed Department of Bioresource Engineering McGill University, co-author of chapter 6, she was involved in methodology development, review and editing.
- Dr. Christopher Nzediegwu Department of Bioresource Engineering McGill University, coauthor in chapter 3, 4, he was involved in Methodology, Writing - review and editing.
- Dr. Ramanbhai Patel Department of Bioresource Engineering McGill University, co-author of chapter 3, he was involved in Writing review and editing.

#### Four manuscripts from this thesis are as follows:

**Chapter 3. Ali Mawof,** Shiv Prasher, Stéphane Bayen, Emma C. Anderson, Christopher Nzediegwu, and Ramanbhai Patel (2021, under review). Effects of barley straw biochar and compost on heavy metals transport in soil and uptake by potatoes grown under wastewater irrigation.

**Chapter 4. Ali Mawof**, Shiv Prasher, Stéphane Bayen, and Christopher Nzediegwu (2021). Effects of biochar and biochar-compost mix as soil amendments on soil quality and yield of potatoes irrigated with wastewater. (Published in the Journal of Soil Science and Plant Nutrition). <u>https://doi.org/10.1007/s42729-021-00549-2</u>

**Chapter 5.** Ali Mawof, Shiv Prasher, Stéphane Bayen, and Lan Liu (2021, under preparation). Fate and transport of PPCPs in soil-plant system in the presence of sorbent materials.

**Chapter 6. Ali Mawof,** Kevin J. Wilkinson, Shiv Prasher, Stéphane Bayen, Emma C. Anderson, Eman ElSayed, and Saji George. (2021, to be submitted). Wastewater borne TiO<sub>2</sub>-NP's impact on heavy metal uptake by potato plants receiving synthetic wastewater irrigation.

#### Scientific presentations related to the thesis:

**Ali Mawof**, Shiv Prasher, Stéphane Bayen, Eman Elsayed, Christopher Nzediegwu and Saji George (2019, November). Impact of wastewater borne TiO<sub>2</sub>-NPs on plant uptake of heavy metals. Poster presented at the Society of Environmental Toxicology and Chemistry (SETAC), Toronto, ON, Canada.

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# **Chapter 1: Introduction**

### **1.1 General Introduction**

The last century saw water use grow by almost twice the rate of population increase and the future decade is likely to witness a global water demand increase based on three key facts: (i) population growth; (ii) increasing wealth; and (iii) changing diet preferences. It is not only the global population, estimated to increase to 9.3 billion by 2050 and 10.1 billion by 2100 (FAO, 2017; Wheeler et al., 2015), that puts pressure on water resources, but also the increasingly excessive and careless use of water. While water use increased six-fold over the 20<sup>th</sup> century, the global population only increased three folds (Guppy et al., 2017). Currently, approximately 80 countries in the world are facing water shortages, with 2 billion people having no access to clean water (Alois, 2007). Additionally, with a rise in population as well as increasing urbanization, an estimated 70% of the world's population will be living in cities by 2050, compared to 50% at the present time (DESA, 2014). Accordingly, one can expect a further increase in wastewater discharge. This will require safe and sustainable methods of wastewater disposal, which many cities are currently lacking (DESA, 2014). According to (UNFPA, 2001), developing countries dump 90–95% of all sewage untreated and 70% of industrial waste into surface waters bodies, placing both downstream populations as well as ecosystem functions at great risk. Globally, 80% of wastewater flows back into the ecosystems, without being treated or reused (Corcoran, 2010).

Freshwater is a crucial resource for all the lifeforms (i Canals et al., 2009), but constitutes only about 0.8% of the total accessible water present on earth (Dompka et al., 2002; Gleick, 1993). Freshwater depletion has increased over the past 100 years not only due to rapid

population growth but also with improved standard of living, urbanization, industrialization, and economic growth. Combined with the expected population increase of 9.3 billion by the year 2050 (DESA, 2015) and the subsequent rise in global food demand, the need for fresh water, particularly for irrigation purposes, will get intensified. Irrigated agriculture represents only 20% of the cultivated land but produces 40% of the global food production (Ardakanian et al., 2016).

Agriculture is currently the largest consumer of water globally, and demand for more water is continuously increasing. To satisfy this demand, the logical next step is to utilize wastewater for irrigation. Indeed, Hettiarachchi and Ardakanian (2016) reported that wastewater irrigation is already being practiced around the world, with over 20 million hectares of agricultural land presently irrigated with it and showing a high growth potential. Use of wastewater in irrigation is very common in developing countries and regions because of its nutrient content, relatively steady supply, and its ease of availability. These three characteristics lead to widespread use of wastewater in agriculture, where it can fulfill nutrient requirements for plant growth and reduce or eliminate the use of fertilizers.

Wastewater irrigation has the potential to increase agricultural food production, promote freshwater conservation, and limit the harmful practice of openly discharging untreated wastewater into the environment, as commonly occurs in developing countries (Qadir et al., 2010). Wastewater irrigation can address the issues of: (i) freshwater exploitation, (ii) safe wastewater disposal, and (*iii*) cost-effective food production through irrigated agriculture. However, to prevent contamination and pollution of the surrounding environment, wastewater must be treated to some degree before it can be used as irrigation water source.

Wastewater can contain a combination of *inorganic* heavy metals (Cd, Cr, Cu, Fe, Pb, and Zn) and emerging *organic* contaminants such as Pharmaceutical and Personal Care Products

(PPCPs) (*e.g.*, caffeine, carbamazepine, DEET, diclofenac, and triclosan). Inorganic pollutants, such as heavy metals, are of environmental concern due to their toxicity, persistent and bioaccumulative nature (Alloway, 2012). When present at low concentrations, metals such as Fe, Zn and Cu, have a beneficial role in biological system functions, whereas others such as Pb, Cr or Cd, are toxic to microorganisms and plants (Fatta-Kassinos et al., 2016). Contamination of vegetable production sites with either Cd or Pb increases the risk of adverse health effects for humans whose diet contains plants grown in such areas under long-term use of wastewater irrigation. The level of health risks caused by wastewaters containing heavy metals is indicated by different parameters including the transfer factor (TF), daily intake of metals (DIM), and Health Risk Index (Chaoua et al., 2019). Pharmaceutical products are used world-wide for therapeutic, animal husbandry and other purposes, creating the potential to introduce organic PPCPs into the agricultural soil environment through the reuse of partially treated wastewater for agricultural irrigation and biosolids for soil amendment (Dodgen and Zheng, 2016).

Sewage treatment plants (STPs) can remove some contaminants by adsorption, biological degradation, advanced chemical oxidation, and combined chemical and biological processes (Wang and Wang, 2016). However, these treatments are costly and incapable of processing large volumes of wastewater. Furthermore, STPs in many countries are usually not designed to remove emerging contaminants from wastewater and, consequently, these contaminants are discharged into the environment without much removal (Silva et al., 2012). Furthermore, heavy metals can accumulate in soil and translocate to edible crops upon irrigation with contaminated wastewater. This is concerning as heavy metals pose concentrationdependent health challenges when present in the food chain. Therefore, there is an urgent need to develop cost-effective, efficient, simple and easy-to-use techniques to control the transport and translocation of contaminants through wastewater irrigation. Heavy metals' pollution status and ecological effect are commonly reflected by bioavailability/bioaccessibility or biotoxicity (Shahid et al., 2016). To reduce contaminant bioavailability in soil, appropriate steps are needed. Environmentally, effectiveness in reducing the mobility of organic and inorganic contaminants in soil and water media must be shown at both the laboratory- and field-scale. Due to the barriers to centralized wastewater treatment, some viable options for the safe use of wastewater in irrigation may include amendments to the soil, or minimal treatments of the wastewater, resulting in the reduced uptake of contaminants by crops. Specifically, soil-based amendments such as biochar and compost, and the presence of nanoparticles in wastewater, can be considered as possible approaches to achieve these goals.

A soil-based amendment, Biochar, produced from the pyrolysis of organic waste materials, has shown benefits in water treatment (Abit et al., 2012; Kookana et al., 2011). It has large surface area and pore volume (Ding et al., 2016), thereby favoring the sorption of heavy metals (Nzediegwu et al., 2020a, 2020b). Laboratory- and field-scale experiments have shown that biochar can reduce the movement of organic and inorganic contaminants in soil and water systems (Ahmad et al., 2014; Cabrera et al., 2014; Chen and Chen, 2009; Mohanty and Boehm, 2014). Biochar could also reduce translocation of organic contaminants to crops (Hurtado et al., 2017). Further, both (Beesley et al., 2010; Hurtado et al., 2017) showed that compost, another soil-based amendment used to improve soil structure and soil fertility (Smith and Collins, 2007), could also immobilize inorganic and organic contaminants in polluted soil and reduce their bioavailability. Compost is a stable humus-like substance produced through thermophilic biodegradation of organic materials. Compost can increase the cation exchange capacity of soil, increase pH and improve buffering capacity, degrade and immobilize persistent organic pollutants, and favor the mineralization of inorganic pollutants (Fischer and Glaser, 2012).

Nanoparticles (NPs), materials with particle sizes less than 100 nm, have a very high surface area and exhibit unique behaviors. Studies have showed that nanoparticles present in wastewater can remove heavy metals from water (Engates and Shipley, 2011) and consequently reduce their uptake by plants (Cai et al., 2017). Titanium Dioxide (TiO<sub>2</sub>) NPs have been used for organic pollutant immobilization (Clément et al., 2013; Servin et al., 2012). However, their potential interaction with several contaminants in soil-water systems remains undocumented.

Soil amendment with biochar and compost, derived from feedstock of agricultural wastes, can serve as sorbent materials that could control the mobility of several soil contaminants and reduce their uptake by plants. Furthermore, presence of chemical materials in wastewater, such as nanoparticles (TiO<sub>2</sub>), could interact with contaminants, resulting in their reduced mobility and a lower uptake of contaminants by plants.

#### **1.2 Research Objectives**

The overall objective of this research was to study the impact of biochar, compost and nanoparticles on the fate of heavy metals and emerging organic contaminants in a soil-plant system, irrigated with wastewater.

The specific objectives of this research were as follows:

• To study the effects of two rates of biochar (1% and 3%), alone and in combination with compost (7.5%), on the fate of heavy metals (Cd, Cr, Cu, Fe, Pb, and Zn) in the soil, and to evaluate their impact on plant uptake;

• To evaluate how nanoparticles (TiO<sub>2</sub>), present in the wastewater, could affect heavy metal transport in soil profile, and to evaluate their impacts on heavy metal uptake by plants;

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• To study the effects of two rates of biochar, alone or in combination with compost, on the fate and translocation of emerging organic contaminants (caffeine, carbamazepine, DEET, diclofenac, and triclosan) into field-lysimeter-grown potatoes irrigated with wastewater; and

• To study the effects of two rates of biochar (1% and 3%), alone and in combination with compost (7.5%), on plant growth and potato yield under wastewater irrigation.

### 1.3 Thesis Outline

The format of this thesis is manuscript-based. The first chapter is the general introduction, presenting the background of the research, followed by the objective of the research and the scope of this investigation. The second chapter contains an extensive literature review on the subject matter. It brings forth knowledge gaps that are to be filled through future research needs and perspectives that formed the core of this study. Chapters 3, 4 and 5 present the results of the effect of barley straw biochar alone or with compost mix on heavy metal uptake, soil mobility of PPCPs, and yield components in potatoes under wastewater irrigation. Chapters 6 presents the results of the effect of TiO<sub>2</sub>-NPs mixed with wastewater on heavy metal uptake. Chapter 7 presents a general summary and conclusion of this work. Chapter 8 presents the contributions to knowledge and recommendations for future research work. All the references cited in the thesis are given at the end of the thesis. Appendix contains information pertinent to this research, not included in the chapters.

# **Connecting Statement to Chapter 2**

After identifying the key objectives of the study, it was necessary to develop an overall understanding of the relevant knowledge available in the literature. Accordingly, **Chapter 2** presents a review of global research trends in various fields related to the use of wastewater for irrigation, the major contaminants of concern in the wastewater, and finally, the sorbent materials used in the present research.

## 2 Chapter 2: Literature Review

#### 2.1 **Reuse of Wastewater for Irrigation**

Water scarcity studies (Mancosu et al., 2015) have estimated that, in recent years over 40% of the world's population is experiencing water stress, and within the next 50 years, will face a water shortage. This is the result of rapid population growth, industrialization leading to increased water demand, and a considerable increase in domestic and industrial wastewater. Meanwhile, due to climate change, areas affected by drought and water scarcity are growing daily (Ungureanu et al., 2018). Rapidly expanding concerns in the field of water resource management are pressing societal and geopolitical issues that need to be addressed in order to achieve many of the 17 Sustainable Development Goals (SDGs) (Guppy et al., 2017), particularly SDG 6 i.e., 'Ensure availability and sustainable management of water and sanitation for all.' This is especially true in low-income countries, where inadequate wastewater collection and treatment results in farmers, particularly those in the economically attractive peri-urban interface, facing a scarcity of unpolluted surface water sources. An important strategy to cope with freshwater scarcity is the reuse of wastewater (usually partially treated) (Drechsel and Evans, 2010).

Agriculture is currently the largest consumer of water globally, and this demand is continuously increasing with population growth. In the current environment of changing global agricultural markets, agriculture faces three main challenges: (*i*) meeting the growing demand driven by population increase, by increasing the production of safe and nutritious food, (*ii*) poverty eradication and rural economic growth by generating jobs and incomes, and (*iii*) mitigating the effects of climate change that are already affecting the livelihoods of many people through sustainable management of natural resources and adaptation strategies (FAO, 2017).

Among the activities requiring freshwater resources, irrigation consumes the highest fraction worldwide (~70%); accordingly, a number of countries (*e.g.*, USA, Malta, Cyprus, France, Italy, Jordan and Spain) have implemented wastewater reuse in agriculture and landscaping (Fatta-Kassinos et al., 2016). For countries that already have mature wastewater reuse practices (*e.g.*, Spain and Israel), a positive impact on water stress was observed. Being a substitute for fresh water, wastewater can serve to address this global water deficit by contributing to agricultural irrigation, as traditional irrigation is unable to meet the ever-growing irrigation requirements.

Countries most affected by water shortages are expected to account for about 20 % of the global increase in water scarcity brought on by climate change. The impacts will include a decline in water availability, and heightened probabilities of droughts and floods. The world's most vulnerable regions are western Asia and sub-Saharan Africa (Wheeler et al., 2015). Thus, there is a dire need for a greater use of efficient, economical, and environmentally acceptable methods to manage irrigation water use and rehabilitate polluted waters and degraded soils (Wheeler et al., 2015). As previously stated, wastewater can present both a resource and a problem. Wastewater (vs. freshwater) agriculture can prove more economical as it simultaneously performs the dual purpose of water and nutrient replenishment (Nzediegwu et al., 2019a). The use of wastewater for irrigation, particularly untreated wastewater, has become a "blessing in disguise" for farmers, who have reported the following benefits arising from its use (Hettiarachchi and Ardakanian, 2016): (i) the possibility of greater yields due to the high nutrient loading of the wastewater, (ii) lower fertilizer costs and increased income, and (iii) lower energy costs to pump water from groundwater wells. In fact, over 20 million hectares of arable land is already receiving wastewater globally (Jaramillo and Restrepo, 2017). However, whether this reuse can adversely affect humans and ecological systems are issues that need to be identified and assessed (Trimble, 2007). Though it may act as a source of plant nutrients and organic matter, wastewater may also contain undesirable chemical constituents and pathogens that pose several potential environmental and health risks. A number of risk factors have been identified in the reuse of wastewater, with some having short term impacts (*e.g.*, microbial pathogens) and some longer-term impacts that increase with the continued use of wastewater (*e.g.*, salinity effects on soil) (Shakir et al., 2017).

Both positive and negative health effects of irrigating with wastewater can be observed. In poor areas, achieving food security reflects the positive effects of wastewater irrigation, as its use provides a possible (and often the only way) to produce food, promote better nutrition, and increase both income and quality of life. However, due to the presence of pathogens and toxic chemical compounds in wastewater, negative health effects can also be seen (Shakir et al., 2017).

### 2.2 Contaminants in Wastewater

#### 2.2.1 Emerging Organic Contaminants

#### **2.2.1.1** Pharmaceutical and Personal Care Products (PPCPs)

A class of organic contaminants that can seep into the soil via wastewater irrigation and cause negative health effects are Pharmaceutical and Personal Care Products (PPCPs). Pharmaceuticals are prescription, over the counter or veterinary therapeutic drugs used to prevent or treat human and animal diseases, while personal care products (PCPs) are used mainly to improve the quality of daily life (Boxall et al., 2012). For the purposes of this study, a number of PPCPs were selected and analyzed.

**Caffeine (CAF; CAS Number: 58-08-2)** is a commonly used stimulant (Aydin and Talinli, 2013). It primarily enters the environment through sewage effluent; it is excreted in human urine or through residential waste (Sui et al., 2015). It may rapidly degrade in natural environments, especially those rich in bacteria (Knee et al., 2010). Caffeine is highly soluble in

water and likely to persist with low biological activity (Zhang et al., 2013a). Only sorbing strongly onto sandy loam soil (or equivalent sediments), caffeine is therefore likely to infiltrate and cause groundwater contamination (Sui et al., 2015). Secondary and tertiary wastewater treatments (*e.g.*, anaerobic membrane bioreactors, activated sludge treatment) can effectively remove CAF (Sui et al., 2015); however, due to general lack of such treatments at wastewater treatment plants (WWTPs), wastewater contains CAF. Studies showed that caffeine is taken up by plants, especially aquatic plants, and can be metabolized into plant tissues (D. Q. Zhang et al., 2013a). However, Malchi et al. (2014) reported that it could also be taken up by root crops irrigated with wastewater. Basic compounds can partially dissociate to form cationic and neutral forms. Basic polar PPCPs, like caffeine, can enter roots due to electrical attraction between cations and the negatively charged cell (Wu et al., 2015). Hurtado et al. (2017) showed that biochar could reduce plant uptake of CAF and other organic contaminants.

**Carbamazepine (CBZ; CAS Number:298-46-4)** is a dibenzadiazepine derivative commonly used as an anticonvulsant and psychotic stabilizer (Kosjek et al., 2009). Entering the environment primarily through wastewater effluents and agricultural biosolids, CBZ is also found in groundwater due to its low sorption and rate of degradation (Sui et al., 2015). Persistent in the environment, CBZ's retention times in groundwater can be up to 8 years (Drewes et al., 2003). As a highly polar compound that lacks functional groups and sites for soil and sediment sorption (Kosjek et al., 2009), CBZ may accumulate in soils with high organic matter content (Paz et al., 2016; Sui et al., 2015). Absorbed CBZ is then readily available for plant uptake as it is easily desorbed by water (Paz et al., 2016). Biochar, due to its affinity to organic molecules, is able to immobilize many PPCPs including CBZ (Williams et al., 2015). Carter et al. (2014) found that CBZ was taken up to a great extent by both radish (*Raphanus sativus* L.) and ryegrass (*Lolium perenne* L.) (52 and 33 µg g<sup>-1</sup>, respectively). Malchi et al. (2014) found that CBZ and

several other pharmaceutical compounds were taken up by root crops irrigated with untreated wastewater.

A polar compound of low volatility (Eggen et al., 2013; Trapp, 2009), soluble in both organic solvents and water (Weeks et al., 2012), **DEET** (**N**, **N-Diethyl-3-methylbenzamide; CAS Number: 134-62-3** is the primary active ingredient of several insect repellents (Sui et al., 2015). Insecticides and insect repellents can enter aquatic ecosystems via wastewater effluent, air spray or surface waters, or through the application of biosolids in agriculture (Weeks et al., 2012). It is often found in surface and ground waters adjacent to sewage treatment plants or septic systems (Del Rosario et al., 2014), as well as in ground and surface water (Tran et al., 2014). It is retained primarily in receiving waters and soil (Weeks et al., 2012), and is moderately mobile within the soil column. DEET can be removed by ozonation, microfiltration, anaerobic, anoxic, aerobic and UV processes (Wang et al., 2015a). Wu et al. (2014) also observed high concentrations of DEET in the treated wastewater and the uptake of cucumbers and bell peppers compared to the other organic contaminants analyzed, indicating that DEET is very likely to accumulate in vegetation when present in high concentration.

**Diclofenac (DCF; CAS Number: 15307-79-6)** is a widely used anti-inflammatory and pain-relieving drug. The second most prescribed drug in Germany in 2004 (Stülten et al., 2008), DCF has been detected extensively in wastewater effluent and water bodies throughout Europe (Stülten et al., 2008). Diclofenac is a fairly recalcitrant molecule and is therefore not fully eliminated during wastewater treatment. It has been found in wastewater effluent at levels found above the limit of detection (LC-MS/MS) (Vieno and Sillanpää, 2014). Diclofenac has been found in surface waters, generally at concentrations less than 100 ng/L, however, concentrations of around 8.5  $\mu$ g/L were found in a river water in Pakistan where untreated wastewater was

discharged (Vieno and Sillanpää, 2014). Zhang et al. (2008) concluded that WWTPs could not remove carbamazepine and diclofenac effectively. The removal efficiency of carbamazepine is less than 10% in most cases while that for diclofenac varies from 0% to 80%, but mainly remains in the range of 21–40%. A number of studies (Inyang and Dickenson, 2015; Jung et al., 2015; Lonappan et al., 2018; Sani et al., 2016) have shown that biochar could adsorb DCF. H. Wang et al. (2012a) found that compost could enhance the degradation of DCF. Schaffer et al. (2015) showed that compost could reduce DCF concentration in soil. Zhang et al. (2012) reported that diclofenac could be translocated into various parts of plants; for example, DCF was found in tomato (*Solanum lycopersicum* L.) fruits after prolonged wastewater irrigation (Christou et al., 2017).

**Ibuprofen (IBU; CAS Number: 15687-27-1)** is a widely used nonsteroidal antiinflammatory, analgesic, and antipyretic drug (Scheytt et al., 2005). Ibuprofen mainly enters the environment through wastewater effluent and application of biosolids (Eslami et al., 2015). Ibuprofen enters wastewater since 70-80% of orally taken ibuprofen is excreted as the parent compound or metabolite (Buser et al., 1999). Ibuprofen is highly mobile in water (Eslami et al., 2015). Barnes et al. (2008) analyzed groundwater samples from 47 sites for 65 organic wastewater contaminants and detected at least 35 contaminants, including ibuprofen, in samples from 81% sites. Eslami et al. (2015) found non-steroidal anti-inflammatory drugs, including ibuprofen in surface water, drinking water and from wastewater treatment plants; they attributed the presence of these drugs to inefficiency of WWTPs. Ibuprofen has an affinity to remain in the aqueous phase and does not strongly sorb to soil and sludge (Eslami et al., 2015); therefore, it is mainly found in water, but can also be found in sediments. A number of studies have observed that IBU adsorbs to biochar (Ali et al., 2009; Essandoh et al., 2015; Hurtado et al., 2017). Ibuprofen is taken up by plant roots and translocated to the aerial tissues (He et al., 2017; Zhang et al., 2016); however, because ibuprofen is degraded in the rhizosphere through release of root exudates, uptake and accumulation usually does not occur at high rates.

Triclosan (TCS; CAS Number: 3380-34-5) is a halogenated diphenyl ether (Dann and Hontela, 2011). Widely used as an antimicrobial agent and found in many household items (e.g., soaps, detergents, fabrics, disinfectants, and other personal care products), TCS represents an emerging health concern because of its metabolites' carcinogenicity, its activity as an endocrine disruptor, its induction of antibiotic resistance, and its effects of skin irritation and increasing rates of allergies. Soluble in a wide range of organic solvents, in aquatic ecosystems TCS exists in a non-ionized form, which is considered more toxic than its ionized form (Dann and Hontela, 2011). Large quantities of TCS end up in wastewater treatments plants but suffer from low removal efficiency. Accumulating in the environment, TCS has been detected in surface waters, solid sediment, soil, and biosolids, as well as in tissues of aquatic animals and humans. Its high octanol-water partition coefficient indicates that TCS is slightly lipophilic, indicating a potential for bioaccumulation in fatty tissues. In laboratory studies, the half-life of TCS in soil was 14 and 70 days under aerobic and anaerobic conditions, respectively (Behera et al., 2010). TCS was found in edible parts of agricultural crops such as carrots, pumpkin (*Cucurbita pepo* L.), zucchini (Cucurbita pepo L.), switchgrass (Panicum virgatum L.), and soybeans [Glycine max (L.) Merr.], when these were grown in soils contaminated with TCS (Macherius et al., 2012).

### 2.2.1.2 Female Hormones

Livestock facilities currently use large doses of growth regulating hormones to enhance animal growth, a significant fraction of which are excreted and contribute to estrogen pollution. The concentration of steroidal estrogens in dry solids ranges from 6-426 ng/g (Biswas et al., 2013). Manure and bio-solids from such livestock facilities are applied to agricultural lands as a form

of organic fertilization (Adeel et al., 2017). Accordingly, in the natural environment steroidal estrogens are mainly found in soil and water bodies situated close to STPs and farms where manure from livestock facilities is applied as a fertilizer. These contaminants are most often seen in soil-water, runoff, groundwater and surface waters (e.g., rivers, lakes and estuaries) (Adeel et al., 2017).

Estrogens are biologically active female reproductive hormones that are produced naturally by human and animals (*e.g.*, estrone-E1, estradiol-E2, and estriol-E3) or synthesized for use in the contraceptive pill [*e.g.*, Ethinyl Estradiol (EE2)] (Adeel et al., 2017). Further contaminant compounds include endocrine-disrupting chemicals. These can mimic agonists and antagonists of estrogen and androgen receptors, thereby potentially stimulating receptor-dependent responses or influencing the expression of estrogen-dependent genes (Wu et al., 2013). Reports have shown links between estrogen in the environment and breast cancer, as well as changes in the reproductive and immune systems of many aquatic organisms (Huang et al., 2014).

The removal of estrogen hormones from wastewater in treatment plants has been widely investigated (Gabet-Giraud et al., 2010; Joss et al., 2004). Their removal through biological treatment was as high as 90%, showing that hormone molecules to be highly sensitive to the biological treatment. Levels of estrogens as high as 676 ng/L (for E3) were quantified in wastewater treatment plant influent samples, but in effluent were below 60 ng/L (for E1 and E3). Applied and discussed by several authors, further methods to remove estrogens from contaminated waters include biological processes, activated carbon, membrane filtration and advanced oxidation processes (AOPs) (Silva et al., 2012). Not surprisingly, each removal option has advantages and limitations (Silva et al., 2012). Contaminants can translocate to crops from

contaminated soil or wastewater irrigation. The uptake of estrogen by plants is passive or active depending on the environment, with accumulation potentially occurring in roots and/or shoots, though most steroid hormones are accumulated in the roots. Wetland macrophytes, leafy vegetables, alfalfa, poplar, maize, and willow are plants that have been reported to take up and accumulate steroidal estrogens (Bircher, 2011). Zheng et al. (2016) found that hormones (E1, E2, and EE2) were detected in lettuce roots even at a very low exposure concentration; however, accumulation in tomato tissues was negligible. Karnjanapiboonwong et al. (2011) found a greater accumulation of EE2 in bean roots than leaves. Similar findings were also reported by Cantarero et al. (2017) for wheat. Card et al. (2013) found E2, E3 and two synthetic estrogens in maize seedlings.

Biochar has been shown to effectively adsorb many organic compounds including persistent organic pollutants [*e.g.*, POPs: PCDD/DFs, PCBs, PAHs] and emerging organic pollutants [*e.g.*, EOPs: PAEs- dibutyl phthalate and di(2-ethylhexyl) phthalate; estrogenic steroid hormones: estradiol, estrone] used as pesticides or in industries as solvents, additives, pharmaceuticals or personal care products (*e.g.*, trimethoprim, triclosan) (Zhang et al., 2013b). Biochar's high surface area, micropore volume and numerous polar functional groups, allows it to take up hormones through sorption (Zhang et al., 2013b). The adsorption capacity of biochar for organic pollutants is influenced by its pyrolysis temperature; a greater sorption occurred with higher production temperatures (Zhang et al., 2013b). This may be attributable to greater pyrolysis temperatures resulting in greater biochar surface area and microporosity, allowing for more effective sorption. Even small amounts (0.1%) of biochar in soil have been able to reduce the bioavailability of certain organic contaminants (Zhang et al., 2013b). Sarmah et al. (2010) evaluated the use of biochar as a soil amendment to retard and degrade estrogenic hormones E2 and E1 in a dairy farm soil treated with biochar originating from three different feedstocks (*e.g.*,

corn cob, pine sawdust, and green waste) at two different application rates (0.5% and 1%) in a batch sorption experiment. The 1% pine sawdust-amended soil a greater sorption ability for hormones E2 and E1 than a non-amended control.

Compost can contribute to the remediation of many natural and anthropogenic organic pollutants, including steroid hormones (Kästner and Miltner, 2016). Compost can act as a biostimulation and bio-augmentation agent, as it provides for a diversity of microorganisms by providing nutrients for their growth and organic matter to act as a growth stimulant (Kästner and Miltner, 2016). Thus, compost could help remediate steroid hormones by assisting their degradation (Kästner and Miltner, 2016). However, it has been posited that organic matter in soil can suppress the sorption of organic contaminants onto biochar through competition for micropore space (Zhang et al., 2013b). Therefore, it is important to understand interaction of biochar and compost in soil affecting immobilization and translocation hormones.

#### 2.2.1.3 Herbicide (Metribuzin)

Metribuzin, commonly employed in pre-emergence weed control or in post-emergence broadleaf weed for potato, soybean, sugarcane, vegetable, and fruit production. (Bouchard et al., 1982; Locke and Harper, 1991; Pauli et al., 1990), is widely used in North America (Fairchild and Sappington, 2002). One of its formulations, SENCOR® 75 F, is a common herbicide approved for use in Canada.

Metribuzin belongs to endocrine-disrupting compounds (EDCs) (Fry and Toone, 1981). It is harmful to human and animal health, and aquatic life. Metribuzin is readily transportable in the soil as it is weakly adsorbed by soil (Sharom and Stephenson, 1976). Majumdar and Singh (2007) showed that an application of animal manure and fly ash increased the receiving soil's metribuzin sorption capacity and significantly reduced leaching losses.
Metribuzin has been shown to readily translocate from the roots of a plant to its leaves (Frear et al., 1983; Hilton et al., 1974). Although Abusteit et al. (1985) showed that tetraploid plants are capable of rapid transformation of absorbed metribuzin to nontoxic products, diploid plants are incapable of inactivating absorbed metribuzin. Metribuzin can be translocated in tuber crops, such as potatoes. Gawronski et al. (1985) found that metribuzin uptake by potatoes increased with its field application rate, and that it accumulated in stems, petioles, and leaf veins of the tolerant cultivar (cv. Russet Burbank), whereas interveinal leaf tissue was the major accumulation site in the susceptible cultivar (Chipbelle). Potatoes are in direct contact with soil and water, and therefore metribuzin in soil or irrigation water may greatly affect their quality.

Soil itself can reduce the concentration of metribuzin (Jebellie and Prasher, 1998; Jebellie et al., 1999; Liaghat and Prasher, 1996; Liaghat et al., 1996), leading to a decrease in translocation. Moreover, soil amendments can change metribuzin dynamics in soil. Biochar has a high sorption capacity for metribuzin, although this capacity varies with feedstock, production temperature and residence, and ageing (Li et al., 2015; Yavari et al., 2015). A biochar amendment to soil can therefore increase the half-life of metribuzin (White et al., 2015), prolonging the presence of metribuzin residues in soil. Strong bonding of metribuzin decreases its microbial degradation, but also decreases its bioavailability to plants (Yavari et al., 2015). Therefore, soil amendment with biochar would have two conflicting effects from an agricultural production perspective; bioavailability of pesticides to the food crop would be reduced, but the efficiency of weed control would be reduced.

## 2.2.1.4 Uptake and Accumulation of PPCPs in Plants

The fate and rate of accumulation of PPCPs into plants vary according to the plant type, maturity, and crop species (Calderón-Preciado et al., 2012), being generally high for underground 'root' vegetables (e.g., potatoes, carrots) that are in close contact with soil and water, but less in fruits (*e.g.*, tomatoes, apples (*Malus domestica* Borkh.)) (Trapp and Legind, 2011).

In evaluating IBU, CAF, and CBZ contaminant uptake and transportation in cucumber (*Cucumis sativus* L.) and tomato plants, Goldstein et al. (2014) found that the physiochemical nature of the contaminant was a major determinant of its rate of uptake into crops, particularly those grown in clay soils with low organic matter. They further found that non-ionic contaminants accumulated at higher concentrations in leaves than in fruit, and ionic contaminants the opposite. Negatively charged contaminants were accumulated at higher levels in crops grown in sandy soil. In evaluating the relationship between PPCP sorption and soil components, several studies have shown the impact of soil organic matter (**SOM**) on non-ionic compounds uptake, but only a limited number of them have shown the effect of soil properties on PPCP uptake by plants (Böhmer, 2007; Pan and Xing, 2013).

Investigating the fate and uptake of pharmaceuticals in soil plant systems, Carter et al. (2014) found the greatest CBZ uptake to occur in radish and ryegrass, whereas uptake was below the limit of quantification. This result showed that the uptake of pharmaceuticals can be related to their hydrophobicity, which explains the different in pharmaceutical uptake by two plant species. Malchi et al. (2014) also found both nonionic pharmaceuticals CBZ, CAF lamotrigine, and ionic pharmaceuticals DCF, ibuprofen, and metoprolol in carrot and sweet potatoes [*Ipomoea batatas* (L.) Lam.]. Dodgen et al. (2013) determined the uptake of four PPCPs (DCF, bisphenol, and naproxen by lettuce (*Lactuca sativa* L.) and collards (*Brassica oleracea*). Similarly, Dodgen et al.

(2015) measured plant accumulation and translocation of 16 PPCPs in 3 plant species (carrot, lettuce, and tomato).

# 2.2.1.5 Physicochemical Parameters for Emerging Organic Contaminants

The uptake the contaminants from soils into plant and their fate can be influenced by physiochemical properties (e.g., solubility in water, octanol-water partition coefficient, organic carbon partition coefficient and acid dissociation constant), environmental characteristics (*e.g.*, soil type, temperature, and soil moisture content in soil), and plant characteristics (*e.g.*, root system, leaf shape and size and lipid content) (Colon and Toor, 2016).

The physical and chemical form of the compounds in the contaminated soil strongly influences the selection of the appropriate remediation technique. Information about the physical characteristics of the site as well as the type and level of contamination at the site must be collected to accurately assess site contamination and remedial alternatives. Among these characteristics are metal loads, the size distributions of particles, and metal species distribution (Wuana and Okieimen, 2011).

The fate of organic contaminants in soils is mainly dependent on their physicochemical properties, which influences their mobility, persistence, and bioavailability in the soil matrix. As physiochemical properties of organic containments vary widely, so does their fatein plant-soil systems.

The octanol-water partition coefficient ( $K_{ow}$ ) and dissociation constant, as indicators of how hydrophobic a compound is, as well as its tendency to adsorb to soil, are among the most useful chemical descriptors of organic contaminants in terms of plant uptake and distribution (Arslan et al., 2017; Colon and Toor, 2016). If a compound is too hydrophilic, it will be unable to enter and cross hydrophobic lipid membranes. In contrast, for compounds of high lipophilicity, adsorption or "solution" in the lipid material occurs, reducing the compound's ability to cross the root's endodermis. Organic compounds for which  $0.5 \le \log K_{ow} \le 3.0$  are less hydrophobic and more easily taken up by plants (Arslan et al., 2017). However, if a compound is too hydrophilic, it will be unable to enter and to cross the roots' hydrophobic lipid membranes (Calderón-Preciado et al., 2013). Compound with a higher log  $K_{ow}$  are more lipophilic and often bind to the lipid membranes of plant roots preventing their uptake (Arslan et al., 2017; Wu et al., 2015). Hence, in general, uptake is most significant for compounds with  $1.0 \le \log K_{ow} \le 4.0$  (Colon and Toor, 2016). There are exceptions to this generalization based on plant type and compound. In general, the rule is only true for neutral compounds. (Goldstein et al., 2014) showed that nonionic contaminants accumulate at higher concentrations in leaves than in fruits, while the vice versa occurred with ionic contaminants. Negatively charged contaminants were accumulated at higher levels when the plant grew in a sandy soil. The authors also reported different contaminants' accumulation in tomato and cucumber fruits and attributed these to differences in fruit transpiration.

 $pK_a$  is the log of the Acid Dissociation Constant, K<sub>a</sub>. A compound's pK<sub>a</sub> is a measure of its strength as an acid, with lower pK<sub>a</sub> values indicating greater acid strength. Studies suggest that basic and neutral organic pollutants are more commonly found in plant tissues than acidic organics, though some have shown greater accumulation of acidic organics in roots (Wu et al., 2013). In soil, acidic PPCPs will partially dissociate to form an undissociated acid and an anion (Trapp, 2009). While anions are resistant to plant uptake, the undissociated acid can rapidly diffuse into roots and then dissociate due to the pH of the plant cell, thus being trapped in the root cell, in what is known as an ion trap (Wu et al., 2015). Examples of compounds that are commonly trapped in roots include diclofenac and ibuprofen. Basic PPCP's are more likely to translocate through stems and leaves (Wu et al., 2015). Further, Goldstein et al. (2014) found that the uptake of acidic pharmaceuticals is further inhibited due to their interactions with dissolved organic matter present in treated wastewater.

The  $\mathbf{K}_{oc}$  is the organic carbon-water partition coefficient. A high value indicates that the compound is strongly sorbed to soil, while a low value indicates the compound is mobile in soil. High sorption of organic compounds in soil can result in their reduced bioavailability (Wu et al., 2015). Investigating the degradation and adsorption of six PPCPs, Triclosan, naproxen, diclofenac, bisphenol A, clofibric acid [2-(4-chlorophenoxy)-2-methylpropanoic acid] and ibuprofen during wastewater treatment processes, Xu et al. (2009) found the biodegradation of PPCPs in soils to follow a first-order exponential decay, with half-lives varying from 0.81 to 20.44 day. The authors also noted that soil clay content and soil organic matter influenced the degradation of PPCPs.

# 2.2.1.6 PPCPs Remediation

PPCPs can be removed by sewage treatment plants using different removal processes (Wang and Wang, 2016), namely:

• *physical*, *i.e.*, use of activated carbon, graphene and graphene oxide, and carbon nanotubes,

• *biological*, degradation with pure cultures, mixed cultures, and through activated sludge processes.

*chemical*, through advanced oxidation processes such as ozonation, Fenton oxidation,
 UV treatment, and ionizing irradiation.

Removal of PPCPs can also be achieved by combining chemical and biological methods (Wang and Wang, 2016). One way of disposing of WWTP sludge contaminated with PPCs is to mix it into construction materials (*e.g.*, cement) to develop a new material (Malliou et al., 2007). Municipal STP (sewage treatment plants) can partially remove these contaminants from wastewater mainly through the use of tertiary treatments such as UV light and ozone treatment (Wu et al., 2013). However, these treatments are expensive, and difficult to apply to large

volumes of contaminated nonpoint source pollution, such as runoff from agricultural land and livestock operations. Moreover, these treatments cannot be used when PPCPs are present in soil.

Soil amendments, such as biochar can immobilize many PPCPs and other organic compounds, including persistent organic pollutants (POPs: PCDD/DFs, PCBs, PAHs) (Zhang et al., 2013b). It also reduces their bioavailability to plants (Williams et al., 2015). They found that biochar amendment decreased PPCP concentrations in soil pore water and also decreased their bioavailability and uptake. Studies have shown that due to its high surface area, large micropore volume and numerous polar functional groups, biochar can adsorb hormones (Zhang et al., 2013b). The adsorption capacity of biochar for organic pollutants is influenced by pyrolysis temperature, with greater sorption being achieved with biochar processed at higher temperatures (Zhang et al., 2013b). This may be the result of higher pyrolysis temperatures leading to increased biochar surface area and micro porosity, allowing for more effective sorption. Even small amounts (0.1%) of biochar in soil have been able to reduce the bioavailability of certain organic contaminants (Zhang et al., 2013b). Due to its affinity to organic molecules, it is able to immobilize many pharmaceuticals and personal care products. A study by Williams et al. (2015) found that biochar amendment decreased the bioavailability and uptake, as well as the pore water concentration of selected pharmaceuticals, including CBZ. Indeed, they found pore water concentrations to be reduced by 34-72%, while plant tissue concentrations were reduced by 17-64%. Sorption of the PPCPs to the biochar's surface was deemed the prime mechanism of these reductions (Williams et al., 2015).

Compost can contribute to the remediation of many natural and anthropogenic organic pollutants (Kästner and Miltner, 2016). Compost can act as a bio-stimulant and bio-augmentation agent, as it provides a diversity of microorganisms, nutrients for their growth, and

organic matter to act as a stimulant (Kästner and Miltner, 2016). Thus, compost could help remediate organic contaminants by assisting in their degradation (Kästner and Miltner, 2016). However, it has been posited that organic matter in soil can suppress the sorption of organic contaminants onto biochar through competition for micropore space (Zhang et al., 2013b). Therefore, it is important to understand the interaction of biochar and compost when used in combination as a soil amendment, particularly regarding the immobilization and translocation of PPCPs.

Recent studies have shown that nanoparticles are effective in immobilization of heavy metals and promote the degradation of organic contaminants. Previous studies on PPCP removal using TiO2 nanoparticles have focused on photochemical reactions (Belet et al., 2019; Liang et al., 2019). Hydroxyl radicals are known as one of the strongest oxidative species that act as a reactive intermediate between organic compounds and photocatalysts (Xiang et al., 2011). Their effects on transport of contaminants in soil and their translocation into food crops under wastewater-irrigated food production system, however, needs to be evaluated. Potential applications of phyto-nanotechnology have shown varied results depending on different toxicity endpoints (e.g., cytotoxicity and genotoxicity). For example, while  $TiO_2$  nanoparticles can enhance crop photosynthesis capacity and nitrogen metabolism, they can also cause antioxidant stress (Wang et al., 2016a) Application onto agricultural soils of WWTPs biosolids, originating from domestic and industrial wastewater, amended with metal oxide nanoparticles, has led to nanotoxicity problems in soil-plant-terrestrial systems (McShane, 2013). With the application of metals in nanoforms, a large range of nanoparticles have emerged in the environment in recent decades. The danger of nanoparticles exists when two metals in different forms may not only harm the soil-plant system, but also may protect plants from one other. For example, Zn salts

reduces cadmium toxicity, but in other forms (Zinc-oxide), Zn increases the negative effects of cadmium (Haisel et al., 2019).

## 2.2.2 Heavy Metals

#### **2.2.2.1 Environmental Occurrence and Pathways**

Heavy metals, elements of high atomic weight and with a density exceeding that of water, occur naturally. Applications employing heavy metals in industries and agriculture have a role in promoting their distribution within the environment, increasing concerns regarding their adverse effects on human health and the environment. Heavy metals, such as Chromium (Cr), Cadmium (Cd), Lead (Pb), Iron (Fe), Zinc (Zn) and Copper (Cu), as well as those we did not study, Arsenic (As), Nickel (Ni) and Mercury (Hg), are called such because they have relatively high densities.

Heavy metals belong to the transition element group of the periodic table. Although they occur naturally in the environment (Environment-Canada, 2012), their occurrence can also be traced to anthropogenic sources (Mohan et al., 2011). Volcanic activity, atmospheric deposition and weathering of rock are sources of naturally occurring heavy metals (Islam et al., 2016). Anthropogenic sources of heavy metals include industrial emissions, refineries and smelters, wastewater, pesticides, petroleum products, electronic products, urban runoff and fertilizers (Islam et al., 2016). They can be found in dissolved form in water as well as in particulate matter form. Karvelas et al. (2003) found that most Ni and Mn were found in a dissolved phase (80%-93% and 65%-85% respectively) whereas Cu, Cr, Pb, Cd, and Zn were mainly found in particulate phase (75%-95%). Lead exhibits the highest association with particulate matter (>95%) whereas iron exhibits only moderate association (58%-75%). Heavy metals are not biodegradable, and thus accumulate in the environment (Adriano, 2001); therefore, it is necessary to remove heavy metals from wastewaters and agricultural land.

Adverse effects of heavy metals on crops/ human/ animal/ aquatic life are dependent on the species, though all pose a serious threat due to their ability to bioaccumulate and persist in nature. Many heavy metals are essential micro-nutrients. However, their intake in excessive amounts has been associated with the reduced immune function, growth retardation, upper gastrointestinal cancer, malnutrition psychological effects (Iyengar and Nair, 2000; Türkdoğan et al., 2003).

# 2.2.2.2 Plant Uptake of Accumulation of Heavy Metals

Heavy metals can be taken up by plant species; however, uptake is dependent on soil composition, water, metal permissibility and absorption availability of the species (Islam et al., 2016). Uptake of heavy metals by plants is quantified using an accumulation factor, which is the ratio of the concentration of heavy metals found in plants to that found in soil (Islam et al., 2017). Heavy metals have been found to accumulate in both plants and animals (Islam et al., 2017), which poses a threat to those consuming these as foods.

In investigating the fate of heavy metals in plants, (Tőzsér et al., 2017) showed that, over a period of 36 months, Cd, Pb, and Zn accumulated in all willow (*Salix* sp.) tissues. Further, several studies have reported interactions between various heavy metals influencing their bioaccumulation; for example, (Vassilev et al., 2005) showed that Cd inhibited the uptake of Zn, Mn, and Cu, but stimulated Fe uptake of Fe in willow roots. In contrast, (Tőzsér et al., 2017) found a significant positive correlation between the accumulations of Cd and Zn in willow stems. Additionally, similar findings were reported by (Han et al., 2010).

# 2.2.2.3 Heavy Metals Soil Remediation

Soil washing, immobilization, bioremediation, and phytoremediation techniques are among the commonly available technologies demonstrated to be effective at the removal of heavy metal

contaminants (Evanko and Dzombak, 1997). In spite of these options being cost-effective and eco-friendly, field applications of these remediation methods have only been employed in a limited number of developed countries and are yet to become commercially available. With an increase in governmental and scholarly studies on the effects of heavy metals in contaminated soils and their implications for the environment, there has been an increasing interest among the scientific community to develop technologies for remediation of contaminated sites. (Bolan et al., 2008).

Other techniques classified for the remediation of heavy-metal-contaminated soil include excavation and disposal, electro kinetic extraction and immobilization (Evanko and Dzombak, 1997; Mahdavi et al., 2015a). Although these methods could also prove environment friendly, field applications of some methods have only been done in a few developed countries and have yet to become commercially available in most developing countries. Soil remediation by excavation and washing or electro kinetic extraction at an agricultural field scale is practically impossible. Immobilization and stabilization of heavy metals in soil through the use of amendments that reduce the mobility and bioavailability of heavy metals may be appropriate for agricultural land (Mahdavi et al., 2015b).

Mulligan et al. (2001) concluded that, of the various remediation techniques, physical containment is the least expensive approach; however, this leaves the contaminants in place without treatment. Since metals are considered relatively immobile, methods for metal decontamination have focused on solid-phase processes such as solidification/stabilization and vitrification, procedures that can be performed *in situ*, thereby reducing handling costs. However, long-term stability of the solidified/stabilized matrix remains unknown. Vitrification is expensive but applicable to mixed wastes where few other technologies are available.

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Additionally, for both these techniques, practical field demonstrations are needed. Other techniques include phytoremediation and bioleaching. These are not as well developed but could be used for areas of low contamination, although longer treatment times may be necessary (Mulligan et al., 2001).

The physical and chemical forms of the compounds in the contaminated soil strongly influence the selection of the appropriate remediation technique(s). Therefore, information about the characteristics, concentrations, and distribution of the contaminants as well as characteristics of the soil (*e.g.*, particle size distributions, hydraulic characteristics, heavy metal holding capacity, etc.) are necessary in selecting the remediation technique (Wuana and Okieimen, 2011). Materials examined as possible heavy metal immobilizing agents include phosphates, lime, iron oxides, biosolids, organic waste and combinations of these agents (Mahdavi et al., 2015a). Additionally, emerging amendments for heavy metal remediation include biochar, compost and nanoparticles.

Given its high surface area, biochar has a high capacity to adsorb heavy metals and organic pollutants (Zhang et al., 2013b). Biochar is typically alkaline, which helps to raise soil pH and stabilize heavy metals, thus reducing their uptake by crops (Zhang et al., 2013b). Biochar generally improves the soil's cation exchange capacity soil and can therefore often remediate heavy metal contaminated soil through heavy metal exchange with cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> (Zhang et al., 2013b). This exchange aids co-precipitation and inner sphere complexation of heavy metals with the functional groups at the biochar surface (Ahmad et al., 2014; Zhang et al., 2013b). However, the effectiveness of this mode of remediation is dependent on both the soil conditions and cations present in both the soil and biochar. Mineral components of biochar such as phosphates and carbonates can also stabilize heavy metals through co-

precipitation, thereby reducing their bioavailability (Zhang et al., 2013b). Both the feedstock and pyrolysis temperature of biochar affects its structure, composition, and pH. These characteristics affect its ability to immobilize and stabilize heavy metals. By binding heavy metals, biochar could also reduce translocation of heavy metal into crops (Tucker and Carson, 1985). Khan et al. (2017) found that amending the soil with biochar at a rate of 5% (w/w) significantly reduced the Cd concentration of the pak choi (bok choy) plant compared to an unamended rate of 2.5%, but the effect varied with different biochar feedstocks.

Compost is also commonly used to reduce the bioavailability of metals in soil (Zhang et al., 2013b). Compost has been shown to reduce heavy metal bioavailability in soil through coprecipitation and immobilization through sorption, although its optimal effectiveness occurs in acidic soils (Kästner and Miltner, 2016). Fountoulakis et al. (2010) found that compost could significantly decrease the concentration of herbicides resulting in removal efficiencies, namely metribuzin and linuron. Kocasoy and Güvener (2009) observed that compost has high retention capacity for several heavy metals, especially Cu, Zn and Ni.

With particle sizes of less than 100 nm, nanoparticles have a very high surface area and exhibit unique behaviors. Given this large surface area, their high reactivity and unsaturated functional groups, nano-metal oxide nanoparticles can immobilize and remove heavy metals from soil through chemical and physical sorption, co-precipitation and reduction (Mahdavi et al., 2015a). Youssef and Malhat (2014) found that TiO<sub>2</sub> nanoparticles removed Pb, Cu, Fe, Cd and Zn from contaminated water; the highest absorption efficiency was 97% for lead and the lowest was 35% for zinc. Nanoparticles in wastewater may interact with another contaminants when a crop is irrigated with wastewater.

# 2.3 Soil Properties

Cation-exchange capacity (CEC) is a measure of the number of ions that can be absorbed, in exchange, on soil particles' negatively charged sites (Hendershot et al., 1993a). Given its high surface area and CEC, biochar has the potential to immobilize heavy metals and prevent leaching and uptake by plants (Beesley and Marmiroli, 2011). Moreover, amendment with biochar has the capacity to increase a soil's CEC, as it has a greater negative charge and greater charge density than other soil particles, and thus a greater capability to adsorb cations. In agronomic terms, with its high CEC, biochar has been shown to reduce nutrient leaching (Huff et al., 2014).

The measurement of pH represents the acidity or alkalinity of a substance on a logarithmic scale, measured through the concentration of hydrogen ions (Hendershot et al., 1993b). Biochar amendment has been shown to increase soil pH, although its impact is inversely proportional to biochar's ash content. For example, in a field trial, (Castaldi et al., 2011) found that a soil pH increases from 5.2 to 6.7 occurred upon amendment of the soil with 3 kg m<sup>-2</sup> of biochar. With respect to biological activities, different biochar parameters including feedstock, pyrolysis temperature and retention time can impact its pH. In general, however, the increase in soil pH due to the biochar amendment can favor increased microbial activity (DeLuca et al., 2015). In contrast, greater rates of alkaline biochar amendment can impede earthworm activity (Liesch et al., 2010). The pH also has an impact on nutrient availability and the mobility of trace metals within the soil. Increases in soil pH due to soil amendment with biochar have been attributed to an increase in the formation of mineral precipitates and an increase in the specific adsorption of heavy metals (Jiang et al., 2012). Furthermore, increased soil pH amplified hydrolysis of heavy metal cations and lead to the formation of metal hydroxides.

Soil organic matter (SOM) is the organic component of soil and consists mainly of organisms at varying stages of decomposition. The SOM serves as an important source of nutrients in the soil, as it allows for the release N and P to the soil through mineralization (Lambers et al., 2008). By cation exchange, it also functions to retain  $Ca^{2+}$ ,  $Mg^{2+}$  and  $K^{+}$  in the soil and influences the mobility of certain trace metals. Zinc retention is dependent on both pH and SOM, while Cu retention is positively correlated with SOM (Güngör and Bekbölet, 2010). In contrast, SOM is negatively associated with Cd desorption (Covelo et al., 2007). For a given soil pH, a greater quantity of SOM provides a greater sorption capacity that low SOM soils (Diaz-Barrientos et al., 2003). Overall, changes to the microbial communities due to biochar amendment influences SOM cycling within the soil (Liang et al., 2010). SOM also increases the general porosity and aggregate stability of soil, influencing infiltration and physical properties, while providing habitats for vital soil microbes (Lehmann et al., 2011). Biochar application has been shown to increase and stabilize SOM pools through increased soil particle aggregation and soil bulk density (Zhang et al., 2010). For example, Laird et al. (2010) found a 69% increase in soil organic carbon 500 days after biochar application.

Typically defined as organic material small enough to pass through a 0.45 µm filter, dissolved organic carbon (DOC) is an important component of soil fertility (King et al., 2015), through it only represents a small fraction of the total carbon in soil (McDowell, 2003). As organic residues in the soil release DOC, DOC is generally higher in soils with a higher proportion of SOM. Accordingly, soil amendment with biochar can indirectly increase DOC through an increase of SOM. In terms of the immobilization of heavy metals, compost and biochar have been shown to result in the co-mobilization of metals with DOC (Beesley et al., 2010).

Nitrogen immobilization and mineralization during the decomposition of organic matter is closely tied to the ratio of the mass of carbon within the organic matter to that of nitrogen (*i.e.*, the carbon to nitrogen (C: N) ratio) (Yamakura and Sahunalu, 1990). The C: N ratio is a measure of the quality of organic matter, rather than quantity (Yamakura and Sahunalu, 1990). A soil's C:N ratio is as function of topography, soil parent material and nitrogen content of the soil organic matter. Mineralization is especially important for plant health, as faster decomposition increases the rate at which nutrients are made available for uptake by the vegetation. Biochar has been shown to increase the C: N ratio of soil; for example, (Paetsch et al., 2018) showed that a soil amendment of maize biochar at rate of 3 kg m<sup>-2</sup> increased a soil's C: N ratio of soil from 9.8 to 15.7-16.5.

# 2.4 Remediation

## 2.4.1 Soil Amendments

## 2.4.1.1 Biochar

Biochar, the carbon-rich solid residues obtained from the thermal breakdown (Inyang et al., 2016) or pyrolysis of organic (usually plant) materials (Lehmann, 2009), has shown some environmental benefits in water treatment (Abit et al., 2012; Kookana et al., 2011), and other applications. Laboratory- and field-scale experiments have shown that biochar application is effective in reducing the movement of organic (Cabrera et al., 2014; Chen and Chen, 2009) and inorganic contaminants in soil and water (Ahmad et al., 2014; Mohanty and Boehm, 2014).

Biochar is effective in the adsorption of many organic compounds (Zhang et al., 2013b). Studies have shown that due to its high surface area, micropore volume and numerous polar functional groups, biochar can uptake steroid hormones through sorption (Zhang et al., 2013b). Biochar of organic pollutants is influenced by pyrolysis temperature, with sorption increasing with higher temperatures (Zhang et al., 2013b). This may be due to higher pyrolysis temperatures leading to greater surface area and microporosity, allowing for more effective sorption. Previous studies have shown that wood-derived biochars have a high sorption affinity to progesterone, significantly decreasing its leaching in soil (Alizadeh et al., 2016).

Biochar produced at high carbonization temperatures has large surface areas and pore volumes (Ding et al., 2016), making it more attractive to heavy metal ions, which physically sorb onto the char surface, and are retained within the pores (Ding et al., 2016; Kumar et al., 2011). Since biochar is mostly negatively charged, positively charged metals can easily be attracted through electrostatic attraction, with ligand specificity and complex formations occurring when various functional groups on biochar either react with different heavy metals (Dong et al., 2011; Wang et al., 2015a) or precipitates out of the solution as a solid mineral (Inyang et al., 2012). Physical (surface sorption) describes the diffusional movements of metal ions into sorbent pores without forming chemical bonds (Ding et al., 2016). Another mechanism that can be involved in the removal of heavy metals can occur through an exchange dissolved metal species of the ionizable cations/protons on biochar surfaces (Ahmad et al., 2014). Electrostatic attraction occurs between the charged surface of biochar and metal ions (Zhou et al., 2014). Biochar can also reduce translocation of heavy metal to crops. Having amended heavy-metal-contaminated paddy field soils with biochar at rates of 0, 10, 20, and 40 Mg ha<sup>-1</sup>, Cui et al. (2013) found that biochar was effective in reducing heavy metal concentrations: compared to non-amended soils, the cadmium (Cd) and lead (Pb) acid-soluble fractions dropped by 15.3-26.7% and 18.2-30.9%, respectively, while their reducible fractions declined by 13.5% to 25.6% and 21.9% to 23.53%, respectively.

Biochar can also reduce the translocation of organic contaminants. Hurtado et al. (2017), determined the effects of different biochar rates (0, 2.5, and 5%) on organic contaminants uptake by lettuce plant. They found 20–76% lower concentrations in biochar-amended soil relative to control. The use of biochar at 2.5% reduced the organic contaminants in lettuce (Hurtado et al., 2017). Beesley et al. (2010) studied the influence of both biochar and compost on bioavailability and toxicity of inorganic and organic contaminants in polluted soil. Their results showed that application of both amendments increased Cu and As concentration in soil by more than 30-fold. The researchers also found that biochar use was more efficient and resulted in a 10-fold decrease of Cd concentration in pore water in soil.

Yang et al. (2016) found that increasing the application rate of rice straw biochar from 1% to 5% decreased the extractable (mobile) heavy metals in the soil and was highly correlated to soil pH. Increased pH can impact metal mobility in soil by promoting the formation of precipitates such as Cu (OH)<sub>2</sub> and Pb<sub>5</sub> (PO<sub>4</sub>)3OH. It can be hypothesized that decreasing the mobility of heavy metals in the soil will decrease the proportion of heavy metals available for plant absorption and uptake. In contrast, Huang et al. (2018) found that although application of different rates of biochar made from Hibiscus cannabinus L., chicken manure, and sewage sludge did reduce stem concentrations of Pb, Zn, Cu, Cd and As in Cassia alta L. grown on multi-metal tailings, there was no significant difference in effectiveness observed between application rates (0.4%, 1% and 3% w/w). Overall, more work is needed to understand the mechanisms through which biochar reduces plant uptake of heavy metals.

# 2.4.1.2 Compost

Compost is used as a soil amendment to increase soil organic matter and improve soil structure and soil fertility (Smith and Collins, 2007). It can increase the soil's CEC, increase pH, improve buffering capacity, as well as degrade and immobilize pesticides and persistent organic pollutants. Compost can increase the soil's microbial diversity by providing food for heterotrophic organisms. Microbial species are reported to aid in increasing the mineralization rate of pollutants (Fischer and Glaser, 2012). Similarly, compost can absorb heavy metals, and reduce their solubility, thus reducing their toxicity to plants. Due to its high surface areas, compost is also able to adsorb highly crystalline minerals.

Compost can act to reduce organic pollutants, such as PPCPs, through a combination of bio stimulation and bioaugmentation (Kästner and Miltner, 2016). Additionally, the literature indicates that compost could effectively remove contaminants such as herbicides and heavy metals. Investigating the effect of a compost amendment on two soil-borne herbicides over a period of 80 days, Fountoulakis et al. (2010) showed that the concentration of both herbicides decreased significantly, with removal efficiencies of 99-100% and 96 % for Linuron and Metribuzin, respectively. Kocasoy and Güvener (2009) determined the retention capacity of compost for several heavy metals (Cu, Zn, Ni, and Cr) at initial concentrations ranging 100 to 1000 mg L<sup>-1</sup>. They found compost to exhibit a high retention capacity for Copper, Zinc, and Nickel but not for Chromium. Their study also suggested that a compost contact time of one-hour is sufficient to efficiently remove the metals.

In a study of the impact of wood-derived biochar (oak, ash, sycamore, and birch) and green waste compost (GWC) soil amendments on heavy metal (Pb and Cu) mobility and uptake by ryegrass, it was found that a mix of both biochar and GWC led to the greatest increase in soil alkalinity (Karami et al., 2011). Furthermore, they found that the combination of compost and biochar had a greater impact on reducing Cu in soil pore water than compost alone but did not have as great of an impact as biochar alone. The compost-biochar combination effected comparable reductions in pore water Pb as compost, while biochar alone was found to be ineffective in this case. In terms of plant uptake, compost alone had the greatest impact on reducing the transfer of Pb from soil to plants, while biochar alone had the least impact. Conversely, biochar amendment alone led to the greatest reduction of Cu in ryegrass, whereas compost resulted in the worst. Overall, for lead, GWC and GWC with biochar reduced the transfer coefficients sharply (Karami et al., 2011).

## 2.4.2 Presence of Nanoparticles in Wastewater (TiO<sub>2</sub>-NPs)

Nanoparticles present in wastewater may have an effect on contaminant mobility in soil and their uptake by plants. In line with this, nanotechnology, a water-based amendment, has grown in importance as a potential technology for environmental remediation. With a considerable surface area, nanoparticles have unique properties and potential applications in reducing the adverse effects of heavy metals on natural resources (Dickinson and Scott, 2010; Shen et al., 2009).

While nanoparticles such as Kaolin, montmorillonite, hydroxyapatite, Fe<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be cost-effective in reducing plant toxicity to heavy metals (Wang et al., 2012b), few studies have focused on their potential ability to alleviate heavy metal-induced root growth inhibition and oxidative stress (Lin et al., 2012; Wang et al., 2012b). Nanoparticles in magnetic form (Fe<sub>3</sub>O<sub>4</sub>) have been effectively used to adsorb heavy metal ions (Shen et al., 2009). Nano-Fe<sub>3</sub>O<sub>4</sub> had substantially beneficial effects on the accumulation of heavy metals in wheat seedlings. Roots have been shown to be the primary site of phytochelatin synthesis and thus of

heavy metal in plants that are not hyperaccumulators of heavy metals (e.g., Cd and Cu) (Zhang et al., 2005). Experiments have also proposed removing heavy metals (copper ( $Cu^{2+}$ ) and cadmium (Cd<sup>2+</sup>) ions) with the aid of nanoparticles (titanium dioxide nanoparticles and methanol). This process has the merit of achieving the same removal efficiency at varying pH scales (Lajayer et al., 2018). Removal of contaminants from paddy fields system by biological soil crusts (BSCs) is well known. However, when the same was combined with Nano-TiO<sub>2</sub>, an increase in the removal of Cd (II) occurred under acidic conditions (Kuang et al., 2020). Studies of the joint toxicity of nanoparticles and heavy metals revealed that nanoparticles decreased metal uptake in rice roots and leaves. In another study, spherical nanoparticles (TiO<sub>2</sub>) exhibited the potential ability to alleviate heavy metal (Cd) toxicity (Ji et al., 2017). However, studies have shown that most of Metal nanomaterials are non-biodegradable and thus remain in the environment for a longer period, leading to changes in soils' physicochemical and biological properties (e.g., pH, toxicity, salinity, organic matter, and natural abundance and diversity of microorganisms). Some nanoparticles, like carbon nanofibers (CNFs), serve as growth stimulants, whereas others show toxic effects on, for example, earthworms (McShane et al, 2013).

## **Knowledge Gaps**

Increasing Fresh-water scarcity, wastewater generation and food demand, are prompting reuse of wastewater for irrigation of food crops in many developing countries. However, several organic and/or inorganic contaminants can be present in these wastewaters. Many developing countries do not have effective wastewater treatment facilities and methods available are either inefficient to remove all contaminants or too expensive, and thus unable to remediate large volumes of wastewater. When contaminated wastewaters are used in irrigation, these contaminants are translocated to edible parts of plants, posing health hazards. Furthermore, contaminants can reach surface and groundwater. Thus, new methods for the safe use of wastewater in agriculture are needed. These new methods need to limit crop uptake of contaminants while being effective, inexpensive, and decentralized. Methods that can either be applied to soil or directly to the wastewater prior to irrigation could be promising.

Biochar and compost amendment to agricultural land may be a viable option, as they have been shown to immobilize several contaminants, reducing their uptake by plants. However, most studies have focused on remediation of one or a very limited number of contaminants. Interaction of various coexisting contaminants could affect their fate in soil and translocation to plants. There is also lack of knowledge regarding the fate of wastewater contaminants' uptake in tuber plants in the presence of sorbent materials, as most studies focus on leafy greens and fruits. Most previous studies evaluated the impact of biochar on plant productivity and contaminants. However, the use of a graded level of biochar as a natural remedy has not been determined for the cocktail of contaminants in wastewater we used for irrigation. A review of the literature showed the effect of compost on the removal of different contaminants. However, effect of compost on contaminant uptake into plant tissues is lacking especially when several organic contaminants and heavy metals are present.

Chemical additives, that can be added directly to the wastewater prior to irrigation, or are already present, may also prove a promising alternative to centralized WWTPs and soilbased amendments. Recent studies have indicated that nanoparticles present in wastewater and can impact the fate of inorganic and organic contaminants. Therefore, the impact of the presence of nanoparticles in wastewater on the uptake of contaminants by plants should be investigated. In terms of organic containments, PPCPs in wastewater can end up in water bodies or soil translocate to crops. While studies have evaluated the uptake by leafy and fruit plants, limited information is available on uptake of several coexisting heavy metals and PPCPs from wastewater by tuber-bearing plants, especially potatoes, which are likely to be exposed to contaminants as the edible parts grow in direct contact with the contaminated soil and/or water. Furthermore, few studies have evaluated PPCPs uptake by long season plants, or their transport in soil to different depths when in contact with a cocktail of synthetic wastewater which also includes heavy metals.

Knowledge of the impacts of NPs in wastewater on irrigated agricultural is lacking from the literature. Current research focuses on the impact of NPs on contaminants within aqueous solutions or with mono-contaminants in soil-plant systems. Research is lacking on the role of NPs in wastewater, when containing a realistic mix of organic and nonorganic contaminants and applied for agricultural irrigation at the field scale.

#### **Connecting Statement to Chapter 3**

The literature review presented in Chapter 2 showed the necessity to investigate the primary literature related to soil amendments research. It presented both a review of current knowledge and an assessment of what additional experimental work would be necessary to thoroughly understand the influence of soil amendments on processes occurring in agricultural soils. Such knowledge would allow us to properly identify the key variables our studies should focus on.

Chapter 3 presents out investigation of the effects of different soil amendments on soil properties and the uptake of heavy metals (Cd, Cr, Cu, Fe, Pb and Zn) delivered by synthetic wastewater irrigation to potato plants. As outlined in Chapter 2, biochar and compost amendments to soil have shown potential as materials capable of adsorbing heavy metals from wastewater delivered to the soil through irrigation. Chapter 3 presents the results of a two-year study designed to investigate the effect, alone or in combination, of soil amendments consisting of agricultural waste biomass (barley straw in this instance) converted to biochar and green and table waste compost. The effects of biochar applied at two amendment rates on heavy metal bioavailability delivered to potato plants grown in a sandy soil in synthetic wastewater were also studied.

The following manuscript (Chapter 3) has been submitted to the journal *Environmental Pollution* and is currently under review. The manuscript is co-authored by Prof. Shiv Prasher, research supervisor, Prof. Stéphane Bayen, research co-supervisor, Ms. Emma C. Anderson, an MSc scholar in the department; Dr. Christopher Nzideguw, a Postdoctoral Fellow at the University of Alberta's Department of Renewable Resources, and Dr. Ramanbhai Patel, a research associate in the department. The original draft has been modified to ensure consistency with the thesis format, and the references cited are listed in the reference section (Chapter 10).

# 3 Chapter 3: Barley straw biochar and compost affect heavy metal transport in soil and uptake by potatoes grown under wastewater irrigation

# 3.1 Abstract

Wastewater can supplement freshwater in agriculture; however, it contains toxic heavy metals such as cadmium, chromium and lead that can be hazardous to humans and the environment. We investigated the effects of barley straw biochar, green and table waste compost, and their mix on heavy metal transport in soil and uptake by potato (*Solanum tuberosum* L.) irrigated with synthetic wastewater for two years. In both years, amending the soil with compost significantly reduced ( $p \le 0.05$ ) cadmium uptake in potato flesh, skin, root and stem; zinc uptake in potato skin and roots; and Cu uptake in potato flesh due to increased soil cation exchange capacity, dissolved organic carbon, and soil pH. Co-amending the soil with compost and 3% biochar significantly reduced ( $p \le 0.05$ ) bioavailability of cadmium, copper and zinc in the contaminated soil. Relative to the non-amended soils, soil amendment with biochar, compost and their mix neither affected the transport of chromium, iron and lead in the soils nor their uptake by potatoes. We conclude that amending soil with barley straw biochar and/or compost produced from city green table waste could serve to improve safety of wastewater irrigated potatoes, depending on biochar application rate and heavy metal type.

**Keywords:** Heavy Metals, Soil Amendments, Plant Uptake, Potatoes, Sandy Soil, Wastewater Irrigation.

## 3.2 Introduction

Wastewater can supplement freshwater demand for irrigation, reduce stress on freshwater resources, and ease the problem of wastewater disposal (FAO, 2013, 2017). However, wastewater contains toxic heavy metals such as arsenic (As), lead (Pb), mercury (Hg) and cadmium (Kunhikrishnan et al., 2012), which are hazardous substances, ranking first through fourth according to the US Agency for Toxic Substances and Disease Registry (ATSDR, 2013). When added to soils through wastewater irrigation, heavy metals are likely to be a greater cause for concern because they can translocate to plant and get to human food chain.

The uptake of heavy metals into plants has been widely studied (Han et al., 2010; Tőzsér et al., 2017; Vassilev et al., 2005). Plants can uptake soluble forms of heavy metals within the root zone and can easily solubilize particle-bound heavy metals with root exudates (Dushenkov et al., 1995; Yang et al., 2005). Plants are capable of accumulating both essential and non-essential heavy metals (Djingova and Kuleff, 2000). Biologically essential heavy metals (oligoelements) include copper (Cu), iron (Fe), nickel (Ni), and zinc (Zn), while non-essential heavy metals include As, Cd, chromium (Cr), Hg, Pb, and tin (Sn). Because heavy metals, especially non-essential, are harmful through all trophic levels, techniques to reduce their mobility and bioavailability in soil and translocation to plants are urgently needed to ensure the safe use of wastewater.

Soil amendments such as biochars have been proposed to reduce the risks associated with using wastewater in agriculture. Biochar is a carbon-rich end-product of biomass pyrolysis with a high capacity to adsorb heavy metals due to its high surface area and abundance of surface functional groups (Jones et al., 2016). Biochar is typically alkaline, which helps raise soil pH and stabilize heavy metals, thus reduce their leaching and uptake by crops (Zhang et al., 2013b). Laboratory and field-scale experiments have shown that biochar amendment has the potential of reducing the movement of inorganic contaminants, such as heavy metals in soil and water systems (Dhiman et al., 2020; Nzediegwu et al., 2019a, 2020b).

Compost, another soil amendment, is a stable, humus-like substance, produced through thermophilic biodegradation of organic materials; it can be used to improve soil structure, increase soil organic matter (SOM) and cation exchange capacity (CEC), thereby improving soil fertility and metal mobility (Smith and Collins, 2007). Kocasoy and Güvener (2009) determined the retention capacity of compost for several heavy metals (Cu, Zn, Ni, and Cr). The authors concluded that compost has high retention capacities for Cu, Zn and Ni, but not for Cr at concentrations ranging from 100 to 1000 mg L<sup>-1</sup>. The greater CEC conferred by compost has been shown to reduce heavy metal bioavailability in the soil through co-precipitation and immobilization through sorption (Beesley et al., 2010; Kästner and Miltner, 2016).

Despite research proving the viability of biochar and compost for the remediation of heavy metals, few studies have examined the impact of different rates of application of biochar (Khan et al., 2017; Kim et al., 2015; Li et al., 2018; Lomaglio et al., 2018) or mixed biocharcompost soil amendments (Egene et al., 2018; Kargar et al., 2015; Oustriere et al., 2017). Moreover, the effectiveness of amending soil with barley straw biochar alone or in combination with compost on heavy metal transport in soil and/or translocation to crops, especially belowground crops prone to contamination through direct contact with wastewater, has not been explored. In addition, mixing barley straw biochar at different rates with compost on heavy metal uptake by tubers has not been reported in the literature. Therefore, we conducted a two-year study to evaluate the effects of two biochar application rates (1% and 3% w/w), when added to soil alone or in combination with compost (7.5% w/w), on the fate of wastewater-borne heavy metals in a sandy soil and their uptake by a potato (*Solanum tuberosum* L.) crop, which comes in direct contact with wastewater in soil.

# 3.3 Materials and Methods

## **3.3.1 Experimental Setup**

The field study was conducted in lysimeters located at the Macdonald Campus of McGill University, Sainte-Anne-de-Bellevue QC, Canada (lat. 45°24'48.6" N, long. 73°56'28.1" W). Polyvinyl chloride (PVC) lysimeters (1 m height  $\times$  0.45 m inner diameter), sealed at bottom with a PVC sheet and provided with a perforated drainage pipe, were filled with a sandy soil obtained from the farm of the Macdonald Campus of McGill University. The properties of the soil prior to its mixing with amendments are given in Table 3.1. Six treatments, in triplicate, were randomly allocated to 18 lysimeters. The treatments were: (i) wastewater control,  $BC_0CP_0$ , (ii) 1% biochar no compost, BC<sub>1</sub>CP<sub>0</sub>, (*iii*) 3% biochar no compost, BC<sub>3</sub>CP<sub>0</sub>, (*iv*) no biochar, 7.5% compost,  $BC_0CP_{7.5}$ , (v) 1% biochar, 7.5% compost,  $BC_1CP_{7.5}$ , and (vi) 3% biochar, 7.5% compost BC<sub>3</sub>CP<sub>7.5</sub>. Prior to the imposition of treatments, soil samples were taken from surface soil and a 0.10 m depth to determine important soil properties affecting heavy metal fate and transport in soil and their uptake by plants, i.e. CEC, DOC, and pH. Compost and biochar were also analysed for heavy metals and nutrients. In the first year, appropriate quantities of biochar and compost (w/w) were thoroughly mixed in the upper 0.1 m of soil in the lysimeters. For two weeks prior to planting, potato seed tubers (cv. 'Russet Burbank') were stored at 8-10°C in a cardboard box covered with cheesecloth, to encourage budding. One potato tuber was planted in each lysimeter with the most prominent bud facing upwards. Nitrogen (N), potassium (K) and phosphorus (P) fertilizers were applied in a ring around the tuber according to the local recommendation rates

for potato. A canvas tent was setup over the lysimeters to prevent natural precipitation from entering the lysimeters. Each lysimeter received 11.5 L of wastewater every 10 days. A total of eight irrigations were applied per season. The concentrations of various contaminants in the synthetic wastewater are given in **Table 3.2.** The concentrations of contaminants were determined based on worst-case scenarios from the global literature on wastewater contamination. Potatoes were harvested 120 days after planting, and their aboveground biomass was separated into stems and leaves.

Mineral components	mg kg <sup>-1</sup>	Soil Properties	
Ν	3.67±0.21	Sand (%)	92.2
Р	74.7±3.52	Silt (%)	4.3
Κ	54.7±6.03	Clay (%)	3.5
Mg	50.0±2.93	рН	5.61±0.19
Ca	754±48.15	SOM (%)	1.82±0.05
Al	1689.2±96.85	EC (mS cm <sup>-1</sup> )	66.43±11.13
Mn	1.9±0.22	ZPC	3.40
Cd	<lod< td=""><td><math>\operatorname{CEC}(\operatorname{cmol}(+)\operatorname{kg}^{-1})</math></td><td>3.35±0.33</td></lod<>	$\operatorname{CEC}(\operatorname{cmol}(+)\operatorname{kg}^{-1})$	3.35±0.33
Cr	21.1±2.81	C (%)	0.82±0.14
Cu	6.8±1.24	N (%)	0.085
Fe	8822±352.14	C: N Ratio	9.61±0.72
Pb	<lod< td=""><td>DOC (mg kg<sup>-1</sup>)</td><td>29.52±2.15</td></lod<>	DOC (mg kg <sup>-1</sup> )	29.52±2.15
Zn	22±5.14	Bulk Density (Mg m <sup>-3</sup> )	1.35

**Table 3.1:** Soil physiochemical properties Prior to Soil Amendments.

SOM: Soil Organic Matter; EC: electrical conductivity; ZPC: Zero Point of Charge; CEC: Cation Exchange Capacity; DOC: Dissolved Organic Carbon; LOD: limit of detection; N, P, K, Mg, Ca, Mn, and Al were determined using Mehlich III extraction (Mehlich, 1984); the heavy metals Cd, Cr, Cu, Fe, Pb and Zn were determined using hot acid extraction (Kargar et al., 2015) and quantified by ICP-OES. Other soil properties were adapted from a previous study conducted with soil from the same field (ElSayed et al., 2013).

Underground biomass was separated into roots and tubers. Potato tubers were peeled to separate flesh and skin. The aboveground biomass (stem and leaves) and underground biomass (root, skin and flesh of tuber) were washed with deionized water and air-dried. Tuber flesh was dissected longitudinally and further diced to about 10 mm cubes, washed and oven dried at 60°C for 48 h. Dried samples were then ground for heavy metals analysis. Soil samples from each lysimeter were collected at the end of each season (2017 and 2018). Soil cores of the top 0.10 m soil layer were sampled at 20-mm intervals after harvesting. After completion of the first year of the experiment, the lysimeters were covered with plastic bags to prevent freshwater from rainfall or snow entering the lysimeter over the winter months. In the second year, amendments were not applied and same lysimeters were used for respective treatments. At the end of the second season, soil samples were also taken from the surface soil and at 0.10-m depth to determine soil properties, such as CEC, DOC, and pH.

## **3.3.2** Physicochemical Characterization of Biochar and Compost

Barley straw biochar was purchased from InnoTech Alberta (Canada). Prior to carbonization, barley straw feedstock was chopped into pieces less than 50 mm long. Pyrolysis was then performed in a Batch Rotary Drum (80" length × 24" diameter) at ~ 535°C for 28 minutes (total retention time: 83 minutes). The final product was cooled under CO<sub>2</sub> gas purging for 2-3 hours. The compost was derived from mixed green and table waste from the city of Baie-D'Urfé in the West Island region of the island of Montreal (QC, Canada). Barley straw biochar and compost samples were subjected to an ultimate and proximate analysis at the CanmetENERGY (NRC) Characterization Laboratory, Ottawa, ON, Canada.

Category	Substance/compounds	Country	Concentration (mg L <sup>-1</sup> )	Reference
C source	Na Acetate	NA	79.37	(Nopens et al., 2001)
	Milk powder	NA	116.19	
	Soy Oil	NA	29.02	
	Starch	NA	122	
	Yeast Extract	NA	52.24	
N Source	NH <sub>4</sub> Cl	NA	12.75	
	Peptone	NA	17.41	
	Urea	NA	91.74	
P Source	$Mg_3O_8P_2$	NA	29.02	
Minerals	CaCl <sub>2</sub>	NA	60	(LaPara et al., 2006)
	NaHCO <sub>3</sub>	NA	100	
Surfactant	Triton X-100	NA	*30	(Aboulhassan et al., 2006)
Heavy Metals	Chromium (Cr)	India	2	(Ahmad et al., 2011)
	Cadmium (Cd)	India	5	
	Lead (Pb)	India	16	
	Iron (Fe)(II)	India	120	
	Zinc (Zn)	India	3	
	Copper (Cu)(II)	India	8	
Hormones	Estrone: E1	S. Korea	*8.15 (20)	(Sim et al., 2011)
	Estradiol: E2	S. Korea	*0.634 (20)	
	Estriol: E3	S. Korea	*2.28 (20)	
	Ethinylestradiol: EE2	China	* 0.33 (20)	(Zhou et al., 2012)
	Progesterone	China	*0.90 (20)	(Huang et al., 2009)
PPCPs	Ibuprofen	Canada	*45	(Guerra et al., 2014)
	DEET	U. S	*6.5	(Lietz and Meyer, 2006)
	Caffeine	China	*6.6	(Sui et al., 2010)
	Carbamazepine	S. Korea	*21.6	(Sim et al., 2011)
	Diclofenac	India	*25.68	(Singh et al., 2014)
	Triclosan	UK	*21.9	(Sabaliunas et al., 2003)
	Oxytetracycline	China	19.5	(Li et al., 2008)

**Table 3.2:** The concentration of heavy metal and organic contaminants in synthetic wastewater

\*Concentrations in  $\mu$ g L<sup>-1</sup>, NA not applicable, numbers in () indicates the concentration used in this work.

The moisture content, ash content, volatile matter and fixed carbon content (ASTM D7582 and ISO 562 for volatiles) were determined by proximate analysis. Levels of C, H, O, N and S were determined through ultimate analysis (ASTM D5373 and ASTM D4239 for S). The heavy metals content was determined in the Bioresource Engineering Department (BED) Laboratory of McGill University, following hot acid extraction (EPA, 1996; Kargar et al., 2015). The P, K, Calcium (Ca), Magnesium (Mg), and Manganese (Mn) levels were determined using Mehlich III extraction (Mehlich, 1984) while N was determined according to the methods of (Carter and Gregorich, 2008). The results of analyses are shown in **Table 3.3.** 

Parameter	Observed Value (%, w/w)		<i>Heavy Metal and Mineral concentrations</i> (mg kg <sup>-1</sup> )			Allowable Thresholds (mg kg <sup>-1</sup> ) *	
	BC	СР		BC	СР	BC	СР
Moisture TGA	3.88	4.38	Cd	<lod< td=""><td><lod< td=""><td>1.40</td><td>20.00</td></lod<></td></lod<>	<lod< td=""><td>1.40</td><td>20.00</td></lod<>	1.40	20.00
Ash TGA	19.29	64.43	Cr	29.80	19.91	64	1060
Volatile	18.19	29.09	Cu	<lod< td=""><td>44.22</td><td>63</td><td>757</td></lod<>	44.22	63	757
Fixed Carbon	62.53	6.47	Fe	706.71	8205.25	NA	NA
Carbon	70.40	18.80	Pb	<lod< td=""><td><lod< td=""><td>70</td><td>505</td></lod<></td></lod<>	<lod< td=""><td>70</td><td>505</td></lod<>	70	505
Hydrogen	2.20	1.83	Zn	33.11	90.01	200	1850
Nitrogen	1.07	1.28	Ν	5.12	36.81	NA	NA
Total Sulfur	0.53	0.16	Р	244.02	763.72	NA	NA
Oxygen	6.47	13.47	Κ	18201.05	4324.15	NA	NA
$SSA (m^2 g^{-1})$	8.5	2.05	Mg	520.23	1008.01	NA	NA
pН	9.61	7.87	Ca	750.09	4991.21	NA	NA
EC (mS cm <sup>-1</sup> )	4302.02	1226.61	Mn	40.02	40.15	NA	NA

**Table 3.3:** Properties of barley straw biochar (BC), and compost (CP)

TGA: thermogravimetric analysis; SSA: specific surface area; EC: electrical conductivity; NA: not available; \* *Based on* International Biochar Initiative allowable thresholds of heavy metals in biochar, and Guidelines for Compost Quality by Canadian Council of Ministers of the Environment (CCME, 2005) (mg kg<sup>-1</sup>).

## **3.3.3 Sample Extraction and Quantification**

Soil analysis was undertaken in the BED Laboratory. Soil DOC was determined using a TOC analyser (Sievers InnovOx Laboratory). CEC was measured using the BaCl<sub>2</sub> method (Hendershot et al., 1993a), while pH measurement, using a pH electrode (Accumet pH meter

model AB15, Fisher, Scientific, USA), followed the method of Rayment and Higginson (1992). The hot nitric acid digestion method (EPA, 1996; Kargar et al., 2015) was used to determine the heavy metals concentration in soil samples and plant tissues.

A homogenized sample of 0.16 g was added to a 15 mL test tube with 2 mL of concentrated nitric acid (trace metal grade, 70% pure). The solution was allowed to equilibrate overnight. Samples were then placed on a block digester (Fisher Scientific®, dry batch incubator), where the temperature was gradually increased to 80°C, and then maintained until any brown colour disappeared. The temperature was further increased gradually to 120±5°C and maintained at this temperature for 5 hours. Samples were removed and cooled for 15 mins. The digested solution was transferred to 50 mL Falcon tubes and diluted to 50 mL with deionized water, before being stored at 4°C until heavy metal quantification. The soil samples were analysed with an inductively coupled plasma Optical emission spectrometry equipment (ICP-OES, Varian, Vista-MPX CCD simultaneous, Varian Inc, Victoria, Australia). Plant tissue samples were analysed with an inductively coupled plasma mass spectrometry (ICP-MS, Varian ICP820-MS, Varian Inc, Victoria, Australia). To ensure quality control, reference materials (SED98-04 and SED92-03, Environment Canada) and blanks were added to all runs.

## **3.3.4 Statistical Analysis**

Heavy metal concentration in soil was assigned as a response variable, and treatment and depth were assigned as fixed-effects variables. The data were analysed using the GLM procedure of SAS 9.4 (SAS Institute Inc., Cary, NC). The concentrations of heavy metals in the plant tissues data and soil physicochemical properties were analysed using a one-way analysis of variance (ANOVA), considering treatment as the only factor and differences were considered significant when p < 0.05.

## 3.4 Results

#### 3.4.1 3.1 Effects of Soil Amendment on Soil Properties

Soil CEC, DOC and pH in the different treatments at surface and 0.10 m soil depth are presented in **Table 3.4.** The bulk soil CEC, before the experiment, was 3 cmol kg<sup>-1</sup> (**Table 3.1**). CEC decreased to 1.78 and 2.62 cmol kg<sup>-1</sup> in BC<sub>0</sub>CP<sub>0</sub> (no soil amendment) at both 0 and 0.10 m depths after two years of wastewater irrigation. Treatments receiving compost for (BC<sub>3</sub>CP<sub>7.5</sub>, BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>0</sub>CP<sub>7.5</sub>) had greater ( $p \le 0.05$ ) CEC at the surface and 0.1 m depth than their respective non-compost-receiving treatments (BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub> or BC<sub>3</sub>CP<sub>0</sub>). At the soil surface, CEC for each CP<sub>7.5</sub> treatment exceeded that of all CP<sub>0</sub> treatments, however, at 0.10 m, only BC<sub>0</sub>CP<sub>0</sub>, and BC<sub>1</sub>CP<sub>0</sub> were differed from CP<sub>7.5</sub> treatments, and only BC<sub>3</sub>CP<sub>7.5</sub> differed from CP<sub>0</sub> treatments. This indicated the addition of 3% biochar is likely increased the CEC. No significant difference in soil CEC was found between BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>0</sub> treatments at the soil's surface or a 0.10 m depth.

Treatments	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )		DOC (	DOC (mg kg <sup>-1</sup> )		pH	
	Surface	0.10 m	Surface	0.10 m	Surface	0.10 cm	
$BC_0CP_0$	1.78±0.29 <sup>b</sup>	2.62±1.24°	13.17±0.85 <sup>d</sup>	12.61±0.75 <sup>b</sup>	$5.00\pm0.10^{d}$	$5.26 \pm 0.14^{d}$	
$BC_1CP_0$	1.69±0.31 <sup>b</sup>	1.88±0.33°	$11.62 \pm 1.18^{d}$	11.68±3.27 <sup>b</sup>	5.18±0.15 <sup>cd</sup>	$5 \pm 0.2^{d}$	
BC <sub>3</sub> CP <sub>0</sub>	1.94±0.44 <sup>b</sup>	$4.12 \pm 1.34^{bc}$	$13.38 \pm 1.67^{d}$	$19.85{\pm}0.20^{ab}$	5.33±0.14 <sup>bc</sup>	6.11±0.03°	
BC <sub>0</sub> CP <sub>7.5</sub>	4.58±0.94 <sup>a</sup>	$7.39{\pm}0.93^{ab}$	27.31±1.06 <sup>a</sup>	24.10±11.36 <sup>a</sup>	5.60±0.10 <sup>a</sup>	6.43±0.3 <sup>bc</sup>	
BC <sub>1</sub> CP <sub>7.5</sub>	$4.60 \pm 1.46^{a}$	5.54±0.29 <sup>b</sup>	23.35±2.69 <sup>b</sup>	24.90±2.45ª	5.43±0.17 <sup>ab</sup>	$6.5 \pm 0.14^{b}$	
BC <sub>3</sub> CP <sub>7.5</sub>	$5.73 \pm 2.74^{a}$	$7.57 \pm 1.60^{a}$	18.33±1.75°	28.43±8.03ª	5.66±0.11 <sup>a</sup>	7.13±0.15 <sup>a</sup>	

Table 3.4: Effects of biochar, compost and biochar-compost mix on CEC, DOC, and pH.

The different letters in each column represent a significant difference at  $p \le 0.05$ ; values are mean  $\pm$  standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.

The DOC of soil before experiment was 29.5 mg kg<sup>-1</sup> (**Table 3.1**). It decreased to 12.89 mg kg<sup>-1</sup> (average of surface and 0.1 m) in BC<sub>0</sub>CP<sub>0</sub> under wastewater irrigation. The DOC at the soil surface was greater ( $p \le 0.05$ ) for the BC<sub>0</sub>CP<sub>7.5</sub> treatment as compared to other treatments, followed by BC<sub>1</sub>CP<sub>7.5</sub> then BC<sub>3</sub>CP<sub>7.5</sub> (**Table 3.4**). Biochar alone treatments (BC<sub>1</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>0</sub>) produced no significant difference (p > 0.05) in DOC compared to the non-amended BC<sub>0</sub>CP<sub>0</sub> (control). At the 0.10 m depth, compost amendment alone or in combination with biochar led to significantly greater ( $p \le 0.05$ ) DOC concentrations than the BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> treatments. The DOC under BC<sub>3</sub>CP<sub>0</sub> was moderate and not significantly different than any other treatment. The results indicate that increased DOC in soil was mainly due to compost. The trends in DOC were similar to CEC, with amendment with 3% (*vs.* 1%) biochar leading to greater CEC.

The initial pH of sandy soil was 5.5 (**Table 3.1**). After wastewater irrigation, the soil pH without amendment BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> was slightly lower than 5.5 in both depths (**Table 3.4**). At the surface or 0.10 m depth, soil treatments of BC<sub>0</sub>CP<sub>7.5</sub>, and BC<sub>3</sub>CP<sub>7.5</sub> had a greater ( $p \le 0.05$ ) soil pH than BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> amendments; no significant differences were observed in pH between BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub>. Soil amendment with 3% biochar clearly increased soil pH at a 0.10 m depth. pH was also significantly increased by compost amendment; BC<sub>3</sub>CP<sub>7.5</sub> showed a greater ( $p \le 0.05$ ) pH value than under BC<sub>3</sub>CP<sub>0</sub> at both depths, indicating that compost had the greatest impact on pH. Similarly, BC<sub>1</sub>CP<sub>7.5</sub> showed a greater ( $p \le 0.05$ ) pH than BC<sub>1</sub>CP<sub>0</sub> at both depths. Overall, pH was significantly higher in compost treatments compared to those without compost, irrespective of biochar content.

Overall, the 7.5% compost amendment significantly increased CEC, DOC and pH. Although 1% biochar amendment had minimal impact on these parameters, the 3% biochar amendment also caused a significant increase in these soil properties. Considering the average between the surface and 0.1 m depth values, it was observed that there was an increase in CEC, DOC and pH by about 0.83 cmol kg<sup>-1</sup>, 3.725 mg kg<sup>-1</sup>, and 0.59, respectively, due to the 3% biochar amendment. On the other hand, the corresponding increase was 4.285 cmol kg<sup>-1</sup>, 12.815 mg kg<sup>-1</sup>, and 0.885 for compost. These values indicate that amendment of 7.5% compost was more effective in increasing these parameters than 3% biochar.

# 3.4.2 Effect of Soil Amendments on Heavy Metals Mobility in Soil

The soil amendments also impacted heavy metal soil mobility. Initial concentrations of toxic (Cd, Cr, Pb) and non-toxic metals (Cu, Fe, Zn) in the soil are given in **Table 3.1**.

Figure 3.1 and Tables (3.5, 3.6, and 3.7) show heavy metal concentrations at the end of both experiments' seasons (2017 and 2018) at 0-20 mm, 20-40 mm, 40-60 mm, 60-80 mm and 80-100 mm depth ranges.

The initial soil Cd concentration was below detection limits (**Table 3.1**). After wastewater irrigation, soil Cd in 2017 was detected at depths of up to 60 mm in BC<sub>3</sub>CP<sub>7.5</sub> plots and of up to 80 mm in all remaining treatments **Figure 3.1** (**A**, **B**). Soil Cd was greatest in the 0-20 mm layer and gradually decreased with depth in all treatments, indicating that Cd slowly leached downward due to irrigation. In the top layer (0-20 mm), the soil Cd was significantly greater ( $p \le 0.05$ ) for compost treatments, with or without biochar, and greater for BC<sub>3</sub>CP<sub>0</sub> soil than the non-amended (BC<sub>0</sub>CP<sub>0</sub>) or BC<sub>1</sub>CP<sub>0</sub> soils. This could be because CEC in compostamended treatments was significantly greater ( $p \le 0.05$ ) than for no-compost treatments. Higher biochar concentrations also had an impact, as CEC for the BC<sub>3</sub>CP<sub>0</sub> treatment was greater than BC<sub>0</sub>CP<sub>0</sub> or BC<sub>1</sub>CP<sub>0</sub>. The Cd in irrigation wastewater can be better adsorbed in a soil with greater CEC. While the soil Cd concentration at 20-40 mm was similar across all treatments, it was significantly greater ( $p \le 0.05$ ) at lower soil depths in BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> than under the other treatments. These results indicate that 3% biochar and compost reduced the mobility of Cd.

In year two (2018), soil Cd was also detected in the 80-100 mm soil layer, indicating that soil Cd continued to move downward with the continued application of wastewater. Again, the soil Cd concentration was lower nearer to the surface (0-20, 20-40, and 40-60 mm) and higher at 80-100 mm in  $BC_0CP_0$  and  $BC_1CP_0$  treatments than under the remaining treatments.

This confirms that compost and 3% biochar impact Cd mobility at the soil surface and in lower soil layers. A larger proportion of soil Cd was adsorbed near the soil surface in the treatments with 3% biochar and/or compost.

While the treatments had a significant influence on soil Cd concentrations, results were inconclusive for Cr and Pb. Concentration of Cr in soil at the end of experiment in both years is given in **Table 3.5.** The initial concentration of Cr in soil was 21 mg kg<sup>-1</sup>. In 2017, there was no effect of amendments on the soil Cr concentration across all depths. Cr concentrations were noticeably higher in treatments with compost although no statistically significant differences were observed. The same trend was observed in 2018 at 40-60 mm and 80-100 mm layers, however, there was no conclusive evidence that compost amendment led to greater adsorption of soil Cr. Overall, as expected that the concentration in 2018 would be higher than 2017 due to the continued application of wastewater irrigation.

Lead was not detected in the soil before the experiment (**Table 3.1**). In 2017, all treatments showed detectable soil Pb layers except the 80-100 mm in depth, but no significant differences were observed (**Table 3.6**). Generally, soil Pb concentration decreased as depth increased, suggesting that Pb moves slowly in soil with application of wastewater. After continued wastewater irrigation in 2018, Pb was detected in the 80-100 mm soil layer and
concentrations decreased with depth. Generally, the soil Pb concentrations were significantly

higher ( $p \le 0.05$ ) in 2018 than in 2017, due to the continuation of wastewater irrigation.

Treatments	0-2 cm	2-4 cm 4-6 cm		6-8 cm	8-10 cm			
	2017							
BC <sub>0</sub> CP <sub>0</sub>	60.10±2.10 <sup>a</sup>	42.42±12.15 <sup>a</sup>	25.67±8.84ª	24.06±1.89 <sup>a</sup>	20.58±1.45 <sup>a</sup>			
$BC_1CP_0$	$60.77 \pm 6.60^{a}$	36.31±5.69 <sup>a</sup>	20.52±2.45ª	25.44±5.62 <sup>a</sup>	21.23±1.06 <sup>a</sup>			
BC <sub>3</sub> CP <sub>0</sub>	64.92±8.78 <sup>a</sup>	32.58±9.89 <sup>a</sup>	23.62±2.35 <sup>a</sup>	$24.48 \pm 4.32^{a}$	19.34±0.64 <sup>a</sup>			
BC <sub>0</sub> CP <sub>7.5</sub>	66.73±21.54 <sup>a</sup>	31.99±4.84 <sup>a</sup>	21.97±1.12 <sup>a</sup>	23.15±3.94 <sup>a</sup>	22.81±1.31 <sup>a</sup>			
BC1CP7.5	90.46±23.38 <sup>a</sup>	31.55±3.96 <sup>a</sup>	24.83±3.52 <sup>a</sup>	26.11±5.63 <sup>a</sup>	22.41±3.44 <sup>a</sup>			
BC <sub>3</sub> CP <sub>7.5</sub>	$90.94 \pm 38.87^{a}$	41.17±13.70 <sup>a</sup>	23.23±1.98 <sup>a</sup>	23.89±5.25 <sup>a</sup>	22.01±5.46 <sup>a</sup>			
			2018					
BC <sub>0</sub> CP <sub>0</sub>	$30.60 \pm 2.78^{a}$	33.02±9.01 <sup>a</sup>	29.51±3.41 <sup>bc</sup>	27.14±2.37 <sup>a</sup>	23.42±2.39 <sup>bc</sup>			
$BC_1CP_0$	34.70±5.34 <sup>a</sup>	32.52±6.44 <sup>a</sup>	32.87±4.63 <sup>bc</sup>	32.65±6.73 <sup>a</sup>	26.55±2.14 <sup>ab</sup>			
BC <sub>3</sub> CP <sub>0</sub>	35.03±9.15 <sup>a</sup>	29.13±3.01ª	26.14±4.08°	24.76±6.30 <sup>a</sup>	22.44±3.11 <sup>bc</sup>			
BC <sub>0</sub> CP <sub>7.5</sub>	39.36±3.52 <sup>a</sup>	$36.04 \pm 6.67^{a}$	41.50±2.85 <sup>a</sup>	35.13±3.30 <sup>a</sup>	24.56±1.14 <sup>ab</sup>			
BC1CP7.5	41.25±8.99 <sup>a</sup>	37.92±2.25 <sup>a</sup>	36.10±5.49 <sup>ab</sup>	39.15±15.97 <sup>a</sup>	28.48±2.17 <sup>ab</sup>			
BC <sub>3</sub> CP <sub>7.5</sub>	37.99±5.65ª	34.30±6.87ª	33.94±6.65 <sup>abc</sup>	36.83±9.34 <sup>a</sup>	$30.89 \pm 7.55^{a}$			

**Table 3.5:** Cr concentration (mg kg<sup>-1</sup>) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean  $\pm$  SD, n = 3.

<sup>a-d</sup> Within year, different letters in the same column indicate a significant difference ( $p \le 0.05$ ).

As for the non-toxic metals, biochar and compost also had no impact on Fe mobility. The initial soil Fe concentration was 8822 mg/kg (**Table 3.1**). The Fe soil concentrations increased due to wastewater irrigation, but there was no significant difference between treatments (**Table 3.7**). In both years, the concentration decreased gradually with depth in all treatments. In 2017, the average concentration was 15724 mg/kg at 0-20 mm, decreasing to 12787 mg/kg at the 80-100 mm depth. In 2018, the corresponding concentrations were 16122 (0-20 mm) and 12832 (80-100 mm) mg/kg, indicating that Fe moved readily from the surface to lower depths in the soil, even beyond 100 mm.

Conversely, the treatments did impact the mobility of Cu and Zn. In 2017, the soil Cu concentration at 0-20 mm was greater ( $p \le 0.05$ ) in the BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub> treatments than in other treatments **Figure 3.1** (**C**, **D**), suggesting that compost, with or without biochar, increased soil Cu adsorption. Similarly, to Cd, when biochar was applied alone, 3% biochar amendment provided greater adsorption of Cu than 1% biochar. The concentration gradually

decreased with depth in all treatments. There was no significant effect of amendments on Cu in the 20-40 mm soil depth. Differences in concentration among treatments in the 40-60 and 60-80-mm depths were observed but the concentrations were relatively low. Cu was not detected at 80-100 mm in 2017.

**Table 3.6:** Pb concentration (mg kg<sup>-1</sup>) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean  $\pm$  SD, n = 3.

Treatments	0-2 cm 2-4 cm		4-6 cm	6-8 cm	8-10 cm	
	2017					
BC <sub>0</sub> CP <sub>0</sub>	292.00±6.88a	172.96±111.01a	10.77±0.82c	28.54±3.75a	<lod< td=""></lod<>	
$BC_1CP_0$	319.80±39.43a	122.97±41.06a	23.53±2.60abc	30.03±22.08a	<lod< td=""></lod<>	
BC <sub>3</sub> CP <sub>0</sub>	354.86±37.47a	109.92±54.42a	32.05±17.91ab	44.51±18.54a	<lod< td=""></lod<>	
BC <sub>0</sub> CP <sub>7.5</sub>	357.89±136.83a	43.85±5.69a	23.68±3.86abc	23.90±7.70a	<lod< td=""></lod<>	
$BC_1CP_{7.5}$	512.71±163.66a	116.12±74.16a	36.34±16.16a	44.21±24.96a	<lod< td=""></lod<>	
BC <sub>3</sub> CP <sub>7.5</sub>	478.87±183.55a	139.99±97.67a	15.78±2.08bc	24.60±19.00a	<lod< td=""></lod<>	
		2	2018			
$BC_0CP_0$	366.91±75.91b	131.77±113.43a	144.45±150.17a	73.84±38.46ab	37.93±29.67a	
$BC_1CP_0$	345.32±45.81b	230.55±259.36a	59.17±47.10a	88.19±75.93ab	38.89±39.80a	
$BC_3CP_0$	383.83±118.61b	131.31±134.81a	42.78±29.08a	29.13±21.77b	7.60±2.83a	
$BC_0CP_{7.5}$	456.28±180.58b	179.42±72.22a	178.48±88.65a	87.25±50.13ab	23.01±16.62a	
BC1CP7.5	556.85±166.02ab	330.90±112.52a	167.98±110.62a	163.29±96.02a	110.85±176.82a	
BC <sub>3</sub> CP <sub>7.5</sub>	724.91±133.58a	150.97±110.91a	191.96±62.72a	148.18±18.68a	29.35±33.96a	

< LOD: means below the limit of detection. <sup>a-d</sup> Within year, different letters in the same column indicate a significant difference ( $p \le 0.05$ ).

Conversely, Cu was detected at 80-100 mm depth in 2018, and again, concentrations declined with depth. At the surface soil, the Cu concentration in mixed biochar and compost amended plots (BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub>) was significantly greater than in other treatments. Soil Cu concentrations were slightly greater in 2018 than in 2017 for corresponding treatments; the mean soil Cu concentrations across all treatments were 9, 52, 745, and 353% higher in 2018 for the 0-20, 20-40, 40-60, and 60-80 mm depths. Given that differences in the surface layers were quite low, but substantially larger at the 40-80 mm depths, it appears that adsorption sites in the upper layers were quickly saturated and could, therefore, no longer hold additional Cu. It appears that biochar, alone, is ineffective in preventing Cu transport, but biochar compost mix can bind Cu added through irrigation water.



**Figure 3.1:** Effect of biochar and/or compost amendments on (A, B) Cd, (C, D) Cu, and (E, F) Zn concentration (mg kg<sup>-1</sup>) in different soil layers on the day of harvest in 2017 and 2018. The different letters above bars in a given column represent significant difference at p < 0.05; Error bars are standard error of three replicates.

Trt	0-2 cm	2-4 cm	4-6 cm	6-8 cm	8-10 cm
			2017		
$BC_0CP_0$	15424.44±305.48 <sup>a</sup>	15584.31±410.82 <sup>a</sup>	14815.54±1158.52 <sup>a</sup>	13757.77±879.31ª	12296.06±1384.47ª
$BC_1CP_0$	15638.91±1229.95 <sup>a</sup>	15484.50±423.90 <sup>a</sup>	13184.62±483.58 <sup>a</sup>	14213.65±983.29 <sup>a</sup>	13620.87±934.55 <sup>a</sup>
$BC_3CP_0$	14899.25±707.55 <sup>a</sup>	14082.52±2417.82 <sup>a</sup>	14381.73±1195.88ª	12688.85±2433.57 <sup>a</sup>	11820.13±769.12 <sup>a</sup>
BC <sub>0</sub> CP <sub>7.5</sub>	15707.36±1024.78 <sup>a</sup>	14612.88±642.89 <sup>a</sup>	13335.80±959.10 <sup>a</sup>	12790.16±1299.73 <sup>a</sup>	13514.55±757.46 <sup>a</sup>
BC1CP7.5	16545.92±756.84 <sup>a</sup>	14592.07±468.43 <sup>a</sup>	13356.42±837.48 <sup>a</sup>	13357.83±801.69 <sup>a</sup>	12428.86±247.42 <sup>a</sup>
BC <sub>3</sub> CP <sub>7.5</sub>	16126.18±1051.67 <sup>a</sup>	16235.98±651.43 <sup>a</sup>	13230.18±986.85 <sup>a</sup>	14254.73±2597.80 <sup>a</sup>	13042.83±2498.00 <sup>a</sup>
			2018		
$BC_0CP_0$	15766.43±2054.19 <sup>a</sup>	14398.20±1340.50bc	14795.42±1535.24 <sup>ab</sup>	13468.15±385.03 <sup>ab</sup>	12657.73±631.50 <sup>ab</sup>
$BC_1CP_0$	15589.19±1383.89 <sup>a</sup>	14574.01±1386.05 <sup>b</sup>	14216.98±1453.63 <sup>ab</sup>	14052.59±1426.64 <sup>a</sup>	13623.98±311.68 <sup>ab</sup>
BC <sub>3</sub> CP <sub>0</sub>	15287.49±3444.10 <sup>a</sup>	12887.64±834.86°	13047.33±512.72 <sup>b</sup>	11618.55±577.17 <sup>b</sup>	12117.48±1068.98 <sup>b</sup>
BC <sub>0</sub> CP <sub>7.5</sub>	16938.51±1454.31ª	14872.43±263.44 <sup>ab</sup>	15342.64±1271.16 <sup>a</sup>	13276.33±646.01 <sup>ab</sup>	12677.46±1256.38 <sup>ab</sup>
BC1CP7.5	16477.21±491.24 <sup>a</sup>	16248.04±339.57 <sup>a</sup>	14650.58±1725.93 <sup>ab</sup>	13947.65±1831.53 <sup>a</sup>	13761.56±1047.86 <sup>a</sup>
BC <sub>3</sub> CP <sub>7.5</sub>	16671.64±739.49 <sup>a</sup>	14157.63±411.40 <sup>bc</sup>	14328.70±542.76 <sup>ab</sup>	13680.20±569.25 <sup>a</sup>	12154.92±832.70 <sup>ab</sup>

**Table 3.7:** Fe concentration (mg kg<sup>-1</sup>) in different soil layers on the day of harvest in 2017 and 2018. Values are the mean  $\pm$  SD, n = 3.

<sup>a-d</sup> Within year, different letters in the same column indicate a significant difference ( $p \le 0.05$ ).

As for Zn, in 2017, compost soil amendments increased soil Zn concentration ( $p \le 0.05$ ) in the 0-20 mm soil layer, compared to treatments not receiving any compost **Figure 3.1 (E, F)**. At other depths, no clear trend was observed. In 2018, the effect of compost amendment was evident in the 0-20 mm, 20-40 mm and 40-60 mm soil depths; compost soil amendments increasing ( $p \le 0.05$ ) soil Zn compared to treatments not receiving compost. The soil Zn concentration decreased with depth in all treatments during both years but increased from 2018 to 2017. The mean concentration difference was minimal at the surface layer, but greater with depth, as was also observed with Cu. This suggests that although compost would bind limited amounts of Zn from wastewater, this element will still move deeper into the profile.

# 3.4.3 Effect of Soil Amendments on Heavy Metals Uptake by Plant

The soil amendments also impacted the uptake of heavy metals by the plant. The concentration of heavy metals in both years in potato flesh and skin, root, and stem and leaves are given in **Table 3.8** and **Table 3.9**.

In both 2017 and 2018, Cd concentrations in the flesh and skin of the potatoes was significantly greater in the BC<sub>0</sub>CP<sub>0</sub> treatment, indicating that all amendments decreased Cd in the edible potato parts. In 2017 there were no significant differences in flesh Cd among the amendments; a similar trend was observed in potato skin, although the was greater under the BC<sub>1</sub>CP<sub>0</sub> than the remaining amendment treatments. The Cd concentration in roots was significantly greater ( $p \le 0.05$ ) under the BC<sub>0</sub>CP<sub>0</sub> treatment than the other treatments. The stem concentration was significantly lower under the compost amended treatments (BC<sub>0</sub>CP<sub>7.5</sub>, BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub>), as compared to non-compost treatments, but there were no treatments effects for Cd concentration in leaves.

In 2018, the Cd concentration in flesh was significantly lower ( $p \le 0.05$ ) under compostamended treatments than only biochar or no biochar treatments. The flesh concentration under BC<sub>0</sub>CP<sub>0</sub> was the highest, followed by BC<sub>1</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>0</sub>. In potato skin, the Cd concentration under BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> were significantly higher ( $p \le 0.05$ ) than under other treatments. Overall, Cd concentrations in root and stem under compost-amended treatments were significantly lower than those under the remaining treatments; however, no significant treatment effect was observed in leaves.

These results indicate that compost amendment reduces Cd uptake into the edible portions of the potato, as well as the root and stem. There was slight reduction in Cd uptake with a 3% biochar amendment, but only a minimal effect with 1% biochar amendment. It may be noted that the topsoil Cd concentration in treatments with compost were higher than that under other treatments. Despite this, the uptake was low, which indicates that compost reduced Cd bioavailability while increases soil adsorption.

HM	Treatments	Flesh	Skin	Root	Stem	Leaves
Cd	$BC_0CP_0$	1.50±0.96 <sup>a</sup>	11.29±0.81ª	146.26±16.54ª	14.04±6.53ª	9.70±2.49 <sup>a</sup>
	$BC_1CP_0$	$1.07 \pm 0.37^{ab}$	7.35±3.21 <sup>ab</sup>	68.52±22.33 <sup>b</sup>	$19.48 \pm 7.04^{a}$	$6.12 \pm 1.48^{a}$
	$BC_3CP_0$	$0.74 \pm 0.13^{ab}$	3.02±0.82°	68.33±20.17 <sup>b</sup>	22.18±13.53 <sup>a</sup>	$4.65 \pm 1.53^{a}$
	BC <sub>0</sub> CP <sub>7.5</sub>	$0.63 \pm 0.06^{b}$	2.29±1.48°	43.82±34.73 <sup>b</sup>	$9.98 \pm 4.85^{b}$	$8.28 \pm 5.87^{a}$
	BC1CP7.5	$0.63 \pm 0.10^{b}$	2.12±1.18°	$43.29 \pm 4.74^{b}$	15.69±6.48 <sup>b</sup>	$8.40{\pm}2.49^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	$0.79 \pm 0.16^{ab}$	$5.65 \pm 2.75^{bc}$	54.30±26.96 <sup>b</sup>	$10.44 \pm 4.56^{b}$	$4.77 \pm 1.64^{a}$
Cr	$BC_0CP_0$	0.10±0.00 <sup>a</sup>	$0.27 \pm 0.05^{b}$	2.09±0.13 <sup>b</sup>	$0.42\pm0.00^{ab}$	$2.66 \pm 1.24^{ab}$
	$BC_1CP_0$	$0.25\pm0.17^{a}$	$0.60\pm0.17^{a}$	1.83±0.49 <sup>b</sup>	$0.35 \pm 0.10^{b}$	$0.49 \pm 0.23^{b}$
	$BC_3CP_0$	$0.20\pm0.04^{a}$	$0.21 \pm 0.04^{b}$	$2.62 \pm 0.44^{ab}$	$0.80\pm0.62^{ab}$	$0.75 \pm 0.34^{b}$
	BC <sub>0</sub> CP <sub>7.5</sub>	$0.28\pm0.18^{a}$	0.36±0.09 <sup>b</sup>	$2.22 \pm 1.20^{ab}$	$0.22 \pm 0.10^{b}$	$4.65 \pm 0.66^{a}$
	BC1CP7.5	$0.22 \pm 0.03^{a}$	$0.45 \pm 0.15^{ab}$	$2.73 \pm 1.28^{ab}$	$2.14 \pm 1.77^{a}$	$4.47 \pm 3.46^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	$0.17 \pm 0.09^{a}$	0.44±0.11 <sup>ab</sup>	$3.59 \pm 0.38^{a}$	$0.45 \pm 0.19^{b}$	0.91±0.38 <sup>b</sup>
Pb	$BC_0CP_0$	$0.24 \pm 0.17^{ab}$	$0.41 \pm 0.22^{b}$	27.12±3.02 <sup>a</sup>	2.55±0.19 <sup>a</sup>	$19.54{\pm}10.47^{a}$
	$BC_1CP_0$	$0.08 \pm 0.03^{b}$	1.38±0.59ª	26.46±9.99 <sup>a</sup>	2.51±1.09 <sup>a</sup>	$5.04 \pm 5.36^{a}$
	$BC_3CP_0$	$0.22\pm0.146^{ab}$	$0.39 \pm 0.08^{ab}$	29.29±10.02 <sup>a</sup>	$5.61 \pm 4.08^{a}$	$3.11 \pm 2.06^{a}$
	BC <sub>0</sub> CP <sub>7.5</sub>	$0.04\pm0.01^{b}$	$1.17 \pm 0.95^{ab}$	12.43±1.13 <sup>a</sup>	$1.35{\pm}1.18^{a}$	$21.21 \pm 17.86^{a}$
	BC1CP7.5	$0.35 \pm 0.01^{a}$	$1.34{\pm}0.19^{ab}$	$27.54 \pm 9.80^{a}$	$9.37 \pm 8.68^{a}$	19.69±21.57 <sup>a</sup>
	BC <sub>3</sub> CP <sub>7.5</sub>	$0.29 \pm 0.04^{a}$	1.56±0.24ª	34.01±9.13 <sup>a</sup>	2.50±2.21ª	4.46±2.21ª
Cu	$BC_0CP_0$	$11.61 \pm 1.73^{a}$	$10.9 \pm 2.18^{ab}$	$39.54 \pm 8.80^{a}$	7.61±2.67 <sup>a</sup>	19.00±4.25 <sup>a</sup>
	$BC_1CP_0$	8.76±1.83 <sup>bc</sup>	12.91±2.65ª	39.34±12.23ª	6.16±2.41 <sup>a</sup>	9.73±3.02 <sup>abc</sup>
	$BC_3CP_0$	6.70±0.94°	$8.67 \pm 0.78^{b}$	39.94±12.94ª	7.66±4.43ª	6.24±1.24 <sup>c</sup>
	BC0CP7.5	$8.018 \pm 1.01^{bc}$	$10.47 \pm 2.2^{ab}$	$25.80 \pm 17.57^{a}$	$7.61\pm4.74^{a}$	16.53±10.04 <sup>ab</sup>
	BC1CP7.5	$9.07 \pm 0.50^{b}$	$10.69 \pm 1.5^{ab}$	$30.63 \pm 2.80^{a}$	9.93±6.52ª	15.64±7.28 <sup>abc</sup>
	BC <sub>3</sub> CP <sub>7.5</sub>	6.82±0.79°	$11.64 \pm 2.6^{ab}$	36.94±6.78 <sup>a</sup>	4.51±1.25 <sup>a</sup>	7.36±0.79 <sup>bc</sup>
Fe	$BC_0CP_0$	22.51±5.21ª	77.4±21.06 <sup>a</sup>	405.04±45.93ª	44.01±3.74 <sup>a</sup>	306.97±115.31ª
	$BC_1CP_0$	23.09±7.61ª	$80.16 \pm 29.5^{a}$	$401.97 \pm 185.15^{a}$	46.27±24.10 <sup>a</sup>	190.29±62.08 <sup>a</sup>
	$BC_3CP_0$	$21.55 \pm 0.65^{a}$	$67.10 \pm 23.0^{a}$	375.04±60.40 <sup>a</sup>	69.15±35.61 <sup>a</sup>	145.64±24.21 <sup>a</sup>
	BC <sub>0</sub> CP <sub>7.5</sub>	22.23±1.23 <sup>a</sup>	$51.54{\pm}15.4^{a}$	257.03±54.70 <sup>a</sup>	$24.38 \pm 8.85^{a}$	310.61±212.25 <sup>a</sup>
	BC1CP7.5	27.25±5.38 <sup>a</sup>	55.38±21.3ª	359.00±93.70 <sup>a</sup>	86.21±64.66 <sup>a</sup>	202.26±105.93 <sup>a</sup>
	BC <sub>3</sub> CP <sub>7.5</sub>	23.30±3.80ª	44.66±8.51ª	344.90±42.87ª	32.86±12.27 <sup>a</sup>	162.71±32.01ª
Zn	$BC_0CP_0$	19.61±6.45 <sup>a</sup>	39.39±12.72 <sup>a</sup>	217.36±26.80 <sup>a</sup>	37.95±7.82 <sup>b</sup>	13.97±2.81ª
	$BC_1CP_0$	17.95±2.34ª	32.63±2.78 <sup>ab</sup>	166.16±19.54 <sup>b</sup>	96.06±32.49ª	$9.89 \pm 2.09^{a}$
	$BC_3CP_0$	17.50±2.23ª	21.52±2.04°	87.16±18.35°	55.71±26.20 <sup>ab</sup>	9.93±0.31ª
	BC <sub>0</sub> CP <sub>7.5</sub>	17.95±5.06ª	21.21±7.28 <sup>c</sup>	56.97±0.19°	$65.35 \pm 10.64^{ab}$	13.59±6.09 <sup>a</sup>
	BC1CP7.5	$17.72 \pm 1.16^{a}$	21.22±2.78°	81.26±10.05°	59.38±27.75 <sup>ab</sup>	$11.35 \pm 2.49^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	19.80±4.13ª	25.08±3.98 <sup>bc</sup>	72.25±21.91°	59.00±29.67 <sup>ab</sup>	11.38±0.83 <sup>a</sup>

**Table 3.8:** Heavy metals concentration ( $\mu g g^{-1}$ ) in potato tissues in 2017. Values are the mean  $\pm$  SD, n = 3.

<sup>a-d</sup> Within year, different letters in the same column for a given heavy metal indicate a significant difference  $(p \le 0.05)$ .

Similar to soil mobility, neither biochar or compost (or both) had any effect on the uptake of soil Cr and Pb into potatoes (**Table 3.8** and **Table 3.9**). Exceptionally in 2018, compared to the BC<sub>0</sub>CP<sub>0</sub> control, soil amended with BC<sub>3</sub>CP<sub>0</sub> reduced ( $p \le 0.05$ ) root Cr, but root

Pb ( $p \le 0.05$ ) was greater under BC1CP7.5 than under BC3CP0, BC0CP7.5, or BC3CP7.5. Among Cd, Cr, and Pb, compost appears to be most effective in reducing Cd uptake.

While Cd, Cr and Pb are toxic heavy metals, Cu, Fe and Zn are trace elements required by crops; however, their excessive presence in soil and uptake by plants can be toxic to plants and humans consuming such plants. The concentration of these heavy metals in the plant parts are given in

# Table 3.8 and Table 3.9.

In 2017, the Cu concentration in potato flesh under the non-amendment treatment was significantly greater ( $p \le 0.05$ ) than amended treatments. Moreover, there was significant effect of biochar amendment, and the effect increased with the quantity of biochar; the Cu flesh concentration under the BC<sub>3</sub>CP<sub>0</sub> treatment was slightly lower than under BC<sub>1</sub>CP<sub>0</sub>, and significantly lower under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>1</sub>CP<sub>7.5</sub>. Treatment BC<sub>0</sub>CP<sub>7.5</sub> showed significantly lower soil Cu than the non-amended BC<sub>0</sub>CP<sub>0</sub> treatment; however, there was no difference between BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>1</sub>CP<sub>0</sub>, or between BC<sub>3</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>0</sub>. These results suggest that biochar played the biggest role in reducing in flesh Cu.

In 2018, there were also significantly lower concentration of Cu in flesh for 3% biochar with or without compost than under the remaining treatments, but there was no difference between the two treatments. This indicated that 3% biochar was effective in reducing Cu bioavailability. As was observed in 2017, Cu in leaves was significantly lower under  $BC_3CP_{7.5}$  and significantly higher under  $BC_0CP_0$ , compared to the remaining treatments.

These findings suggest that transport of Cu to leaves may decrease with soil amendments of compost and a high rate of biochar. There was no conclusive difference between treatments for skin, root, and stem for both years.

НМ	Treatments	Flesh	Skin	Root	Stem	Leaves
Cd	$BC_0CP_0$	5.30±1.37 <sup>a</sup>	59.36±19.64 <sup>a</sup>	249.69±43.02ª	24.77±13.18 <sup>ab</sup>	15.35±1.30 <sup>a</sup>
	$BC_1CP_0$	$4.46 \pm 1.79^{ab}$	49.99±6.98 <sup>a</sup>	223.76±45.74 <sup>a</sup>	$30.37 \pm 7.52^{ab}$	$10.58 \pm 1.70^{a}$
	BC <sub>3</sub> CP <sub>0</sub>	3.06±1.33 <sup>bc</sup>	12.61±4.58 <sup>b</sup>	254.31±25.42 <sup>a</sup>	$32.64 \pm 14.64^{a}$	11.84±6.61 <sup>a</sup>
	$BC_{0}CP_{7.5}$	1.30±0.05°	8.32±6.37 <sup>b</sup>	46.31±4.82 <sup>b</sup>	$15.79 \pm 6.10^{b}$	9.90±0.94ª
	$BC_1CP_{7.5}$	1.86±0.57°	7.43±3.95 <sup>b</sup>	76.04±22.56 <sup>b</sup>	15.28±4.13 <sup>b</sup>	$8.85 \pm 2.40^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	1.16±0.21°	$3.98 \pm 0.52^{b}$	100.29±40.45 <sup>b</sup>	14.13±1.03 <sup>b</sup>	$10.10 \pm 5.96^{a}$
Cr	$BC_0CP_0$	$0.04\pm0.01^{a}$	$0.37 \pm 0.04^{ab}$	2.79±0.90 <sup>a</sup>	$0.26 \pm 0.16^{a}$	0.37±0.11 <sup>a</sup>
	$BC_1CP_0$	$0.09\pm0.08^{a}$	0.28±0.01 <sup>abc</sup>	$1.86 \pm 1.04^{ab}$	$0.15 \pm 0.04^{a}$	$0.26 \pm 0.05^{a}$
	$BC_3CP_0$	0.06±0.01 <sup>a</sup>	0.21±0.10°	1.55±0.36 <sup>b</sup>	$0.24\pm0.08^{a}$	$0.27\pm0.14^{a}$
	BC <sub>0</sub> CP <sub>7.5</sub>	$0.04\pm0.00^{a}$	$0.43\pm0.14^{a}$	$1.97 \pm 0.49^{ab}$	$0.06\pm0.01^{a}$	$0.33 \pm 0.07^{a}$
	BC1CP7.5	$0.05 \pm 0.00^{a}$	$0.41\pm0.05^{a}$	$2.48 \pm 0.36^{ab}$	$0.39 \pm 0.37^{a}$	$0.41\pm0.12^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	$0.05 \pm 0.00^{a}$	$0.23 \pm 0.08^{bc}$	1.66±0.16 <sup>ab</sup>	$0.17 \pm 0.12^{a}$	$0.26 \pm 0.08^{a}$
Pb	$BC_0CP_0$	0.03±0.01 <sup>a</sup>	2.32±0.01ª	38.74±18.16 <sup>ab</sup>	0.60±0.32 <sup>a</sup>	2.55±0.19 <sup>a</sup>
	$BC_1CP_0$	$0.04\pm0.02^{a}$	$2.29 \pm 2.25^{a}$	41.72±13.35 <sup>ab</sup>	$1.16\pm0.72^{a}$	2.51±1.09 <sup>a</sup>
	BC <sub>3</sub> CP <sub>0</sub>	$0.04\pm0.01^{a}$	$0.58 \pm 0.21^{a}$	29.00±14.60 <sup>b</sup>	$0.66 \pm 0.97^{a}$	$5.61 \pm 4.08^{a}$
	BC <sub>0</sub> CP <sub>7.5</sub>	$0.03\pm0.02^{a}$	$1.60\pm0.17^{a}$	18.32±6.92 <sup>b</sup>	$0.60\pm0.06^{a}$	$1.35{\pm}1.18^{a}$
	$BC_1CP_{7.5}$	0.03±0.01 <sup>a</sup>	$2.67\pm0.78^{a}$	59.13±21.55 <sup>a</sup>	$0.47\pm0.10^{a}$	$9.37 \pm 8.68^{a}$
	BC <sub>3</sub> CP <sub>7.5</sub>	$0.04\pm0.02^{a}$	$2.56 \pm 2.44^{a}$	25.60±17.98 <sup>b</sup>	$0.80{\pm}0.30^{a}$	2.50±2.21ª
Cu	$BC_0CP_0$	$10.8 \pm 0.97^{ab}$	$23.50 \pm 5.77^{ab}$	72.35±36.61 <sup>ab</sup>	$12.88 \pm 6.34^{a}$	22.21±6.74 <sup>a</sup>
	$BC_1CP_0$	$11.2 \pm 1.24^{ab}$	23.93±5.25 <sup>a</sup>	91.53±45.00 <sup>a</sup>	$11.25 \pm 3.52^{a}$	15.34±1.47 <sup>bc</sup>
	$BC_3CP_0$	8.01±0.71°	15.93±2.15 <sup>ab</sup>	60.92±29.78 <sup>ab</sup>	6.13±4.65 <sup>a</sup>	13.36±2.70bc
	BC <sub>0</sub> CP <sub>7.5</sub>	9.21±1.25 <sup>bc</sup>	22.94±5.81 <sup>ab</sup>	24.37±4.88 <sup>b</sup>	$12.66 \pm 5.44^{a}$	16.19±4.31 <sup>abc</sup>
	BC1CP7.5	12.99±2.31ª	19.72±4.24 <sup>ab</sup>	66.46±32.64 <sup>ab</sup>	$9.25 \pm 1.77^{a}$	18.72±2.52 <sup>ab</sup>
	BC <sub>3</sub> CP <sub>7.5</sub>	6.93±1.05°	$15.49 \pm 3.69^{b}$	32.09±17.66 <sup>b</sup>	6.22±2.51 <sup>a</sup>	12.08±1.22°
Fe	$BC_0CP_0$	26.25±1.37 <sup>a</sup>	134.72±87.14 <sup>a</sup>	1021.98±383.32 <sup>a</sup>	69.18±24.81 <sup>a</sup>	231.93±54.16 <sup>a</sup>
	$BC_1CP_0$	19.1±5.28 <sup>ab</sup>	$83.02 \pm 2.23^{a}$	565.36±87.35 <sup>b</sup>	55.41±40.91 <sup>a</sup>	167.44±23.92 <sup>a</sup>
	$BC_3CP_0$	19.1±3.85 <sup>ab</sup>	$67.17 \pm 34.18^{a}$	580.17±143.41 <sup>b</sup>	28.83±9.04 <sup>a</sup>	166.36±40.59 <sup>a</sup>
	$BC_{0}CP_{7.5}$	$21.03 \pm 6.6^{ab}$	111.76±67.2 <sup>a</sup>	602.66±101.02 <sup>b</sup>	68.00±32.42 <sup>a</sup>	170.29±38.47 <sup>a</sup>
	BC1CP7.5	$23.55 \pm 3.9^{ab}$	70.37±5.19 <sup>a</sup>	963.56±44.25 <sup>a</sup>	$31.58 \pm 6.52^{a}$	195.26±60.15ª
	BC <sub>3</sub> CP <sub>7.5</sub>	18.42±3.02 <sup>b</sup>	42.70±15.68 <sup>a</sup>	529.24±153.27 <sup>b</sup>	$57.32 \pm 22.98^{a}$	166.00±63.28 <sup>a</sup>
Zn	$BC_0CP_0$	26.10±3.51ª	101.46±27.90 <sup>a</sup>	396.82±27.27 <sup>a</sup>	$93.64 \pm 4.38^{a}$	17.14±1.74 <sup>a</sup>
	$BC_1CP_0$	23.83±2.72 <sup>ab</sup>	82.70±9.43 <sup>a</sup>	312.42±51.88 <sup>b</sup>	116.38±64.93 <sup>a</sup>	$15.15 \pm 1.43^{ab}$
	$BC_3CP_0$	20.84±1.59 <sup>b</sup>	41.16±0.20 <sup>b</sup>	307.20±39.76 <sup>b</sup>	$91.52 \pm 45.76^{a}$	11.77±1.36 <sup>bc</sup>
	BC <sub>0</sub> CP <sub>7.5</sub>	$21.15 \pm 2.20^{b}$	$44.65 \pm 7.96^{b}$	115.71±13.23°	$100.11 \pm 37.03^{a}$	13.95±3.28 <sup>abc</sup>
	BC1CP7.5	$22.03 \pm 1.33^{ab}$	$37.77 \pm 4.99^{b}$	115.31±35.20°	$75.08{\pm}14.08^{a}$	13.54±3.12 <sup>abc</sup>
	BC <sub>3</sub> CP <sub>7.5</sub>	19.86±3.86 <sup>b</sup>	$34.88 \pm 12.03^{b}$	122.70±41.77°	$55.88{\pm}18.85^{a}$	10.83±1.92°

**Table 3. 9:** Heavy metals concentration ( $\mu g g^{-1}$ ) in potato tissues in 2018. Values are the mean  $\pm$  SD, n = 3.

<sup>a-d</sup> Within year, different letters in the same column for a given heavy metal indicate a significant difference  $(p \le 0.05)$ .

In 2017, no significant effect of treatment was found on Fe concentration in any potato parts, whereas, in 2018, Fe concentration was significantly lower in flesh and root under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub>. Overall, it there was no conclusive evidence of any effect of soil amendment on bioavailability of Fe in potatoes.

Similarly, there was no effect of amendments on the concentration of Zn in potato flesh, though Zn concentration in skin and root was significantly higher ( $p \le 0.05$ ) in BC<sub>0</sub>CP<sub>0</sub> than in all amendment treatments. In 2018, Zn concentration of potato flesh and skin was significantly lower in treatments with compost and high biochar content than under the non-amended control. Zn concentrations in roots and stems were not affected by treatments, both amendments reduced Zn uptake. Overall, the treatments had the greatest effective on plant uptake of Cd and Cu.

# 3.5 Discussion

#### 3.5.1 Effect of Soil Amendments on Soil Properties and Heavy Metals Mobility

Earlier studies have also shown a compost amendment to improve soil CEC (Egene et al., 2018; Kargar et al., 2015; Oustriere et al., 2017). Compost increases CEC since it increases the soil exchange sites through addition of stabilized organic matter rich in functional phenolic and carboxylic acid groups (Liu et al., 2012; Ouédraogo et al., 2001).

As for biochar, those produced at low (<350°C) temperatures have a higher CEC than biochar produced at higher temperatures due to higher surface area and greater number of oxygen functional groups (Harvey et al., 2011; Huff et al., 2014). Basso et al. (2013) reported applications of 3% and 6% (w/w) of moderate temperature fast pyrolysis (500°C) hardwood biochar had no effect on the CEC of a sandy soil. Our study mirrored these results, soils amended with compost had a greater ( $p \le 0.05$ ) CEC than other treatments, while alone 1% biochar (produced at 535°C) had no effect and 3% biochar had a minimal effect. As for heavy metal immobilization, the application of compost, alone or with biochar, increased the soil CEC, enhancing the retention of metals in topsoil. As a result, though the total concentration of metals in the soil remains unchanged during the remediation process, their bioavailability was substantially reduced due to increased CEC. This concurs with Kargar et al. (2015), who found that soil amendment with compost significantly increases the soil's sorption and retention capacity for trace metals. They suggested that CEC was the main mechanism for controlling the mobility of Cd and Zn in soils. Moreover, Kargar et al. (2015) saw a positive relationship between exchangeable Ca and Mg and compost application rates. Zn and Cd concentrations are negatively correlated with soil leachate's exchangeable cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>), supporting the idea that increased CEC is the main mechanism controlling Zn and Cd mobility (Cavallaro and McBride, 1978).

As the most mobile carbon fraction, DOC plays a crucial role in influencing soil processes like nutrient availability and leaching (Straathof et al., 2014), thereby playing an important role in soil contaminants' mobility and bioavailability (Asensio et al., 2014; Qualls and Richardson, 2003). Soil DOC concentration has been linked to the formation of soluble organo-metallic complexes that may prevent plant's absorption of metals (Egene et al. (2018). Greater DOC has been linked to increased surfaces for metal sorption, reducing the availability of heavy metals to the plants; Beesley et al. (2014) reported that DOC controlled metal mobility after compost amendment. According to Karami et al. (2011), most of the soil's heavy metal pool is complexed by DOC in the presence of compost, and this is more so for Pb and Cu than Zn and Cd. On the other hand, biochar treatment does not enhance metal complexation in pore water to the same extent as compost, which may explain its more effective retention of metals in solid phases. However, compost amendment has also been seen to increase soil Cd, Cu, and Zn concentrations (Egene et al., 2018), which supported our findings that compost amendment enhances the retention of heavy metals in soil.

Soil pH has a strong inverse relationship with trace metals' solubility and mobility (*i.e.*, high pH, low metal solubility; low pH, high metal solubility) (Huang et al., 2014; Zeng et al., 2011), making pH the most significant factor in a metallic element's environmental fate (Harter, 1983; Wang et al., 2013a). Therefore, the soil's pH is key to heavy metal's adsorption, and can take precedence over the complex surface reactions of cations and anions and other metal-binding mechanisms (Beesley et al., 2010; Karami et al., 2011). After mixing compost into soil, the soil pH can increase due to carbon mineralization and the subsequent production of hydroxyl ions by the exchange of ligands and the introduction of basic cations, such as K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2</sup> <sup>+</sup> (Hargreaves et al., 2008), as was shown in this study. Studies have found that biochars, originating from different feedstocks, can also increase soil pH to different extents (Chintala et al., 2014; Khan et al., 2017); the effects of barley straw biochar in our study corroborated their findings.

The pH of the pre-treatment soil and the wastewater were mildly acidic. Compared to the non-amended and 1% biochar treatments, compost and 3% biochar increased soil pH in the root zone (0-100 mm). This concurs with Oustriere et al. (2017) who found that application of biochar together with compost can effectively reduce soil leaching of Cd, Zn, and Pb through increased-pH-driven precipitation–co-precipitation, and various sorption mechanisms. Moreover, in investigating the effects of increasing soil pH, (Friesl-Hanl et al., 2009; Friesl et al., 2006) found that a greater soil pH can promote Pb retention in the soil's solid phase. In our study, CEC, DOC and pH increased when compost, with or without biochar, or 3% biochar alone was amended. Increases in these parameters enhanced adsorption of Cd, Cu and Zn in our study.

Our findings contrast in part with those of Gusiatin and Kulikowska (2016), who reported that sewage sludge compost decreased the bioavailability of soil Cd and Zn, but did not affect the availability of Pb or Cu. Similarly, Tang et al. (2020), found that compost, obtained from agricultural waste, substantially reduced the availability of soil Cd and Zn, but increased availability of soil Cu. In another study, it was found that plantain peel biochar mixed with hydrogel reduce transport of heavy metals, Cd, Cu, Fe and Zn, and retained significantly higher amounts added from wastewater irrigation (Dhiman et al., 2020). Nzediegwu et al. (2020a) also reported that plantain peel biochar significantly increased retention of Cd and Zn in top 0.05 m depth and also retained considerably higher amount of Cr, Cu, Fe and Pb. Dhiman et al. (2020) and Nzediegwu et al. (2020a) attributed the effectiveness of biochar to the higher CEC. Our experiment also indicated that barley straw biochar retained significantly higher amount of Cd in surface. Biochar and compost did not impact the mobility of Cr and Pb in the soil, though they did restrict the mobility of Cd. This is likely attributable to differences in metals' characteristics and competitiveness towards binding sites (Ding et al., 2016; Dudev and Lim, 2014; Park et al., 2016).

It appears that biochar could not restrict transport of Fe, Cu and Zn, minor essential elements for crop growth, although compost exhibited positive effect for Cu and Zn. According to Beesley et al. (2010), the combination of compost with biochar as a soil amendment may be more suitable than biochar alone to promote heavy metal immobilization and buffer nutrient depletion in contaminated soils. Our study showed that barley straw biochar, if applied at the rate of 3%, would reduce transport of Cd, although 1% biochar was not effective. Overall, increase in soil heavy metals retention in amended soil is likely due to the enhancement of the soil physicochemical parameters such as soil CEC, DOC, and pH, such as was associated with compost treatments BC<sub>0</sub>CP<sub>7.5</sub>, BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub> in the present study.

Most of the soil Pb is concentrated in topsoil (0-20 mm), suggesting that Pb adsorption in soils may be permanent and irreversible (Kabata-Pendias, 2000). Although Pb was detected at soil depths of 30-40 mm, 40-60 mm, and 80-100 mm in both years, the concentration was within the permissible limit for Pb in an agricultural soil (< 70 mg kg<sup>-1</sup>) as set by the Canadian Soil Quality Guidelines (CCME, 2007). Although Zn was detected at all soil depths in both years, the concentration was within the Canadian Soil Quality Guidelines permissible limits for an agricultural soil (200 mg kg<sup>-1</sup>) (CCME, 2007).

# 3.5.2 Effect of Soil Amendments on Heavy Metals Uptake by Plant

In terms of bioavailability, our findings are consistent with a reduction in Cd content in dwarf beans (Oustriere et al., 2017) and potatoes (Al Mamun et al., 2017) as a result of compost and biochar amendment, suggesting that a combination of biochar and compost are more efficient in reducing Cd uptake than biochar alone. While the Cd concentration in the flesh of wastewater-irrigated potatoes exceeded the permissible limit of 0.1 mg kg<sup>-1</sup> (Codex, 1995), both BC<sub>0</sub>CP<sub>7.5</sub> and BC<sub>1</sub>CP<sub>7.5</sub> treatments greatly decreased potato flesh Cd in both years compared with the non-amended soil. This is likely a result of the fact that compost is more effective than biochar in reducing Cd translocation in soil.

Alternatively, several studies have looked at the impact of biochar on Cd. Khan et al. (2017) found that the concentrations of Cd in pak choi (*Brassica rapa* ssb. *chinensis* L) was significantly reduced by the addition of 5% (*vs.* 2.5%) biochar, but that the reduction varied according to the biochar feedstock (green tomato waste, chicken manure, duck manure, barley straw, or swine manure). suggesting the importance of determining the optimal quantity of various biochars to apply as a soil amendment, so that crop uptake of heavy metal contaminants is minimized, yet yield is maintained. Our study also saw significant reductions

in skin (2017 and 2018) and flesh Cd (2018) at 3 % biochar, however these impacts were also seen in all treatments with compost. Al Mamun et al. (2017) attributed the decrease in potato flesh Cd to the greater Cd-binding sites on soil incorporated compost, result in a greater soil CEC. The CEC is mainly controlled by surface functional groups.

Kocasoy and Güvener (2009) observed that compost was not effective in adsorbing Cr. Similarly, this study used municipal waste compost and found it ineffective in adsorbing or reducing uptake of Cr. Antonious and Snyder (2007) reported that compost has no effect on Cr concentration in potato tubers in either Cr-contaminated or non-contaminated soils, which highlights those potatoes would take a certain amount of Cr irrespective of concentration in soil. Dhiman et al. (2020) also found no significant effects on Cr concentration in the flesh of potatoes irrigated with wastewater and gown in a soil amended with a polyacrylamide super absorbent polymer alone or mixed with plantain peel biochar.

In terms of Pb, Milojković et al. (2014) also reported that compost produced from aquatic weeds could remove Pb from water. Karami et al. (2011), found a compost and biochar combination showed comparable reductions of Pb in soil pore water, compared to compost alone, while biochar alone was not as effective. In the present study, potato tubers accumulated minimal quantities of Cr and Pb after wastewater irrigation. Also, other studies showed the translocation of soil Cr and Pb to plants to be very poor (Khan et al., 2008; Lee et al., 1981). In contrast to our results, Oustriere et al. (2017) found that both pine bark biochar and green waste compost amendments reduced Pb uptake by dwarf beans, while Eissa (2019) obtained similar results for Old Man Saltbush. This trend was attributed to the fact that Pb was retained in the topsoil and did not move down to the root zone.

In the present study, there was no apparent effect of either barley straw biochar or municipal waste compost on reducing Pb uptake. In 2017 Pb in potato flesh was marginally higher than the permissible limit of 0.1 mg kg<sup>-1</sup> (Codex, 1995).

Concurring with our findings, Chen et al. (2020) reported that soil amendment with compost of wheat straw biochar with different rates reduced bioavailability of Cu. Soja et al. (2018) also reported that biochar was effective in immobilizing Cu, especially in acidic soils. They suggested that the impact of biochar and compost in a Cu-enriched vineyard may depend on either the immobilizing ability of the DOC in the compost fraction or the sorption potential of biochar, in terms of Cu immobilization in the topsoil. However, the soil was mostly acidic in all the treatments, therefore biochar effect was prominent. Generally, there is no effect of compost on Cu dynamics (Wilson, 2017). Kargar et al. (2016) also reported that compost amendment had no significant effects on Cu uptake by barley. Similar to our results, (Seguin et al., 2018) found that Cu bioavailability decreased with the increase of biochar amendment rates. The reduction and Cu bioavailability in the BC<sub>3</sub>CP<sub>7.5</sub> amendment were consistent with the results reported by Jones et al. (2016), who found that soil amendment with biochar and compost significantly reduced the mobility and plant uptake of Cu. Moreover, the most significant reductions in leachable and plant uptake Cu were associated with the greatest biochar application rates in combination with compost.

As with our results, (Nzediegwu et al., 2019a, 2020a) found no effect of plantain peel biochar on translocation of Fe to potato tissues in a two-year wastewater irrigation study. Moreover, similar to our findings, Tahir et al. (2018) found the Fe concentration in spinach to not be affected by biochar amendment or by its co-amendment with different rates of manure. Our findings are contrary to those of (Al Mamun et al., 2017) who found Fe concentration in potato skin to be reduced by amendment of various composts, derived from pig manure, mushroom, sawdust-animal waste, and municipal waste. Likewise, Jones et al. (2016) found three biochar and compost soil amendments to increase Fe concentration in sunflower shoots.

Egene et al. (2018) concluded that although compost amendments could retain Zn in soil and thereby decrease Zn uptake, some decrease in Zn uptake was observed due to both biochar and compost. Similarly, Angelova et al. (2010), found that compost treatment decreased Zn concentration in potato tubers, but had no effect on the other plant parts. Similar reductions in Zn concentrations were also reported for switchgrass by beef cattle manure biochar and compost amendment (Novak et al., 2019) and Chinese cabbage (Awasthi et al., 2019) as a result of soil wheat straw biochar/compost amendment.

Karer et al. (2018) found positive effects of a biochar-compost mix on soil Zn concentration and plant uptake in *Miscanthus*  $\times$  *giganteus* shoots under greenhouse and field conditions. Similarly, Liang et al. (2017) studied the effects of a combination of compost and rice husk biochar at varying application rates on Zn availability. They found that available Zn declined under 10 % and 20 % biochar amendments. The authors related this trend to a pH change under the influence of ratios between both amendments. Overall, the compost and biochar amendments reduced the uptake of Cd, Cu and Zn heavy metals. Compost mainly reduced Cd uptake, whereas barley straw biochar was effective in reducing uptake of Cu. To some extent both compost and barley straw biochar reduced the uptake of Zn.

# 3.6 Conclusions

Soil amendments with barley straw biochar, alone or supplemented with city green and table waste compost, retained wastewater-borne heavy metals in the topsoil, and reduced their uptake by potato plants for two years, depending on biochar application rate and the heavy metal type. Relative to non-amended soils and soils amended at 1%, amending the soils with barley straw biochar at 3% was more effective in reducing heavy metal transport in soil and their uptake by

plants. Amendment with green and table waste compost reduced transport of Cd and Zn relative to the non-amended control and such reduction was further enhanced when the compost was mixed with biochar due to the synergistic effect of the combination. Therefore, co-adding biochar and compost to soil under wastewater irrigation can reduce the potential hazard posed by wastewater-borne heavy metals and ensure metal-free crops.

# 3.7 Acknowledgements

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# **Connecting Statement to Chapter 4**

The study presented in Chapter 3 investigated the effects of biochar and compost as soil amendments, either alone or in combination. Biochar was applied at two rates (1 and 3% w/w). Both amendments' effects on immobilization and plant uptake of heavy metals were investigated. It is additionally necessary to investigate how crop yield is affected by wastewater irrigation and soil amendment. Trials were conducted using the soil amendments and sandy soils used for the experiments described in Chapter 3. The results of this two-year study led to the question of how compost/biochar-amended soils might affect crop growth and yield in a sandy soil irrigated with wastewater.

The following manuscript (Chapter 4) has been published in the *Journal of Soil Science and Plant Nutrition.* The manuscript is co-authored by Prof. Shiv Prasher, research supervisor, Prof. Stéphane Bayen, research Co-supervisor, and Dr. Christopher Nzideguw, a Postdoctoral Fellow at the University of Alberta's Department of Renewable Resources. The original draft has been modified to ensure consistency with the thesis format, and the cited references are listed in the reference section (Chapter 10).

# 4 Chapter 4: Effects of biochar and biochar-compost mix as soil amendments on soil quality and yield of potatoes irrigated with wastewater

# 4.1 Abstract

This study evaluated the impact of biochar, compost and a biochar-compost mix on soil properties and yield of potatoes irrigated with wastewater. In each year of a two-year (2017, 2018) field lysimeter study conducted under wastewater (WW) irrigation, a thrice-replicated completely randomized design (CRD) tested the effect of a factorial combination of 3 levels of barley (Hordeum vulgare L.) straw biochar amendment (none, 1% and 3%) and 2 levels of mixed green and table waste compost amendment (none, 7.5%) on soil physicochemical properties, along with potato (Solanum tuberosum L.) plant growth, physiology and yield components. Relative to the non-amended control, all amendment treatments had a significant positive effect ( $p \le 0.05$ ) on soil physicochemical properties and crop yield; However, amendments did not affect plant growth or plant physiological parameters. Higher temperatures in the second year led to significantly lower yields than in the first year. In 2017, compost alone increased potato yield under wastewater irrigation, whereas in 2018, yield was greater at the 3% biochar amendment rate than at the 1% amendment rate. We conclude that amending soils with biochar and biochar-compost mix is a feasible way to grow potatoes under wastewater irrigation, but application rate and biochar-compost mixing ratio should be properly selected to achieve a high potato yield. Biochar and biochar-compost amendments improved conditions for potato growth under wastewater irrigation, suggesting that wastewater irrigation of crops grown in amended soil may prove a feasible approach to reducing the need to treat wastewater destined for use as irrigation water, while increasing water and nutrient cycling to improve food security.

**Keywords:** Crop Productivity, Sandy Soil, Soil Amendment, *Solanum tuberosum* L, Wastewater Irrigation

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## 4.2 Introduction

Freshwater constitutes only about 0.8% of the total accessible water resources on Earth. Roughly, 80 countries in the world are facing water shortages (Dompka et al. 2002; Gleick 1993), and 2 billion people have no access to clean water (UN 2021). According to the WWF US (2016), two-thirds of the world's population face some type of water stress. Combined with an expected world population of 9.7 billion by 2050 (DESA 2015) and the concomitant rise in global food demand, the need for freshwater for irrigation will be intensified. Increased populations will also lead to increased wastewater discharge necessitating safe and sustainable methods of wastewater disposal, currently lacking in many cities around the world (DESA 2014).

According to UNFPA (2001), developing countries discharged 90–95% of all untreated sewage and 70% of industrial wastewater into surface waters, placing downstream populations and ecosystem functions at great risk. Globally, 80% of wastewaters flows back into ecosystems, without being treated or reused (Baum et al. 2013; Corcoran et al. 2010). While irrigated agriculture currently occupies 20% of cultivated land, it represents an increasing proportion (40% at present) of global food production (IBRD-IDA 2020).

From an economic viewpoint, wastewater irrigation of crops under proper agronomic and water management practices may provide greater yields, additional water for irrigation, and fertilizer savings (Hussain et al. 2002). Accordingly, wastewater irrigation has the potential to increase agricultural food production, promote freshwater conservation, and limit the harmful practice of openly discharging untreated wastewater into bodies of water, then using the latter for irrigation, a common practice in developing countries, where it contributes to the contamination of agricultural soils (Qadir et al. 2010). Wastewater irrigation can also increase soil organic carbon (SOC), nutrient

availability, as well as provide better soil physicochemical and biological properties, including raising soils' available water content, thereby improving soil productivity (Marofi et al. 2015).

Various studies have recorded the positive effects of biochar and biochar-compost mixes on crop yields and soil properties (Kammann et al. 2015; Karami et al. 2011; Seehausen et al. 2017). Soil amendment with biochar and compost can improve crop yields by improving soil pH, increasing soil cation exchange capacity (CEC), supplying nutrients, promoting greater nutrient use efficiency (NUE), and improving water holding capacity (WHC) in sandy soils (Agegnehu et al. 2015; Jeffery et al. 2011). Compared to both wastewater and freshwater controls, soil amendment with either bamboo or bagasse biochar, in combination with wastewater irrigation, significantly increased the biomass yield of energy crops (Ramola et al. 2013). Despite that several studies have amended soils with biochar and compost, the effects of soil amendment with biochar and compost mix on soil and crop parameters are rare, especially in temperate regions (Cooper et al. 2020). Moreover, while few studies have investigated the effects of biochar, and/or compost on the yield of agricultural crops under treated wastewater irrigation (Hameeda et al. 2019), to the best of our knowledge, even fewer studies have addressed the effects of using untreated wastewater to irrigate crops grown in coarsetextured soils amended with different rates of biochar, compost and biochar-compost mix. Therefore, the objectives of this study were to evaluate the impacts of biochar, compost and biochar-compost mix applied to sandy soils at different application rates on (1) soil physicochemical properties and (2) potato yield under untreated wastewater irrigation. We hypothesize that increasing application rates of biochar, compost, or biochar -compost mix would improve plant growth parameters and yield by improving soil physicochemical properties.

#### 4.3.1 Field Setup

A two-year study was conducted in the summers of 2017 and 2018 at the Macdonald Campus of McGill University, Sainte-Anne-de-Bellevue, QC, Canada ( $45^{\circ}24'48.6''$  N latitude and  $73^{\circ}56'28.1''$  W longitude). In the spring of 2017, field lysimeters (1.0 m tall × 0.45 m inner diameter; **Figure 4.1**) were filled with a local sandy soil (**Table 4.1**). After the first season and harvest sampling efforts, the experimental units were protected with plastic bags over the winter until the next season.





The treatment combinations were: (*i*) non-amended soil (WW control) (BC<sub>0</sub>CP<sub>0</sub>); (*ii*) 1% biochar alone, (BC<sub>1</sub>CP<sub>0</sub>); (*iii*) 3% biochar alone, (BC<sub>3</sub>CP<sub>0</sub>); (*iv*) 7.5% compost alone, (BC<sub>0</sub>CP<sub>7.5</sub>); (*v*) 1% biochar and 7.5% compost, (BC<sub>1</sub>CP<sub>7.5</sub>); and (*vi*) 3% biochar and 7.5% compost, (BC<sub>3</sub>CP<sub>7.5</sub>). According to the treatment, biochar and/or compost were thoroughly mixed into the soil, ensuring homogeneity in the upper 0.10 m layer of the lysimeter soil at the onset of the experiments (2017). Compost was added to the soil at a rate of 7.5% (w/w), while biochar was added at rates of 1% or 3% (w/w). The compost and biochar remained in the lysimeters after the first year of harvest and were present at the onset of the second year of experiment.

To determine initial nitrogen (N), phosphorus (P) and potassium (K) levels in the soil, soil samples were taken prior to planting in 2017. In both 2017 and 2018, three fertilizers, *i.e.*, urea, triple super phosphate (TSP), and potassium chloride (KCl), were applied according to locally recommended rates for potato (cv. Russet Burbank). Specifically, N was applied at a rate of 180 kg N ha<sup>-1</sup> (Parent and Gagné 2010); 30% of N fertilizer was applied on day 0, 30% on day 31 after planting, and the remaining 40% in four equal parts on days 46, 53, 60, and 67 post-planting (Stark et al. 2004). Each season, at planting, all treatments received 280 kg K ha<sup>-1</sup> and 44 kg P ha<sup>-1</sup> (Parent and Gagné 2010).

Mineral components	mg kg <sup>-1</sup>	Soil Properties	
Ν	3.67±0.21	Sand (%)	92.2
Р	74.7±3.52	Silt (%)	4.3
K	54.7±6.03	Clay (%)	3.5
Mg	50.0±2.93	рН	5.61±0.19
Ca	754±48.15	SOM (%)	1.82±0.05
Al	1689.2±96.85	EC (mS cm <sup>-1</sup> )	66.43±11.13
Mn	1.9±0.22	ZPC	3.40
Cd	<lod< td=""><td>CEC (cmol(+) kg<sup>-1</sup>)</td><td>3.35±0.33</td></lod<>	CEC (cmol(+) kg <sup>-1</sup> )	3.35±0.33
Cr	21.1±2.81	C (%)	0.82±0.14
Cu	6.8±1.24	N (%)	0.085
Fe	8822±352.14	C: N Ratio	9.61±0.72
Pb	<lod< td=""><td>DOC (mg kg<sup>-1</sup>)</td><td>29.52±2.15</td></lod<>	DOC (mg kg <sup>-1</sup> )	29.52±2.15
Zn	22±5.14	Bulk Density (Mg m <sup>-3</sup> )	1.35

**Table 4.1:** Soil physiochemical properties prior to soil amendments

SOM: Soil Organic Matter; EC: electrical conductivity; ZPC: Zero Point of Charge; CEC: Cation Exchange Capacity; DOC: Dissolved Organic Carbon; LOD: limit of detection; N, P, K, Mg, Ca, Mn, and Al were determined using Mehlich III extraction (Mehlich 1984); the heavy metals Cd, Cr, Cu, Fe, Pb and Zn were determined using hot acid extraction (Kargar et al. 2015) and quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). Other soil properties were adapted from a previous study conducted with soil from the same field (ElSayed et al. 2013).

In both years, prior to planting, SENCOR® 75 F (active ingredient: metribuzin, 4-amino-6*tert*-butyl-3-methylsulfanyl-1,2,4-triazin-5-one), a common herbicide approved for use in Canada, was applied to the soil at the rate of 2.25 L ha<sup>-1</sup> following local guidelines (OMAFRA 2019). Seed potatoes were purchased from Global Agri. Services Inc. (New Maryland, NB, Canada). Potato tubers were stored at 8-10°C on receipt, then warmed to room temperature 2 weeks prior to planting to promote sprouting. On the day of planting, one tuber was planted 0.10 m deep in the center of each lysimeter.

A canvas tent was setup over the lysimeters to prevent precipitation from entering them. To supplement the natural light, 10 LED bulbs (60 W) were installed in an equally spaced array above the lysimeters, and operated 4 hours per day. An Apogee MQ-200 Quantum Flux sensor (Apogee Instruments Inc., Logan, Utah) was used to determine the quantum flux under the tent. Daily weather data for both 2017 and 2018 was collected for the field location (45°25'38.000" N, 73°55'45.000" W) from Environment Canada and averaged for each month of interest (Environment-Canada 2021).

#### 4.3.2 Physicochemical Characterization of Biochar, Compost, and Soil

Barley straw biochar was purchased from Alberta Innovates–Technology Futures (AI-TF) at Vegreville, AB, Canada. Prior to carbonization, the barley straw feedstock was chopped into pieces less than 0.05 m in length. Pyrolysis was performed in a batch rotary drum ( $203 \times 61$  cm) at ~  $535^{\circ}$ C for 28 min (total retention time 83 min). The final product was cooled by purging the drum with CO<sub>2</sub> gas for 2-3 h. The compost used was derived from mixed green and table waste supplied by the West Island region of Montreal, QC (City of Baie-D'Urfé).

Barley straw biochar and compost samples were characterized through an ultimate and proximate analysis. As shown in **Table 4.2**, moisture content, ash content, volatile matter and fixed carbon content (ASTM D7582 and ISO 562 for volatile) were determined by proximate analysis, while carbon, hydrogen, oxygen, N and sulphur contents were determined by ultimate analysis

(ASTM D5373 and ASTM D4239 for S). The analyses of biochar and compost were performed at the CanmetENERGY (NRC) Characterization Laboratory, Ottawa, ON, Canada. The heavy metal content was determined by hot acid extraction (USEPA 1996; Kargar et al. 2015). The P, K, calcium (Ca), magnesium (Mg), and manganese (Mn) concentrations were determined following Mehlich III extraction (Mehlich 1984), while N was determined following the method of Carter and Gregorich (2008). The CEC was measured using the BaCl<sub>2</sub> method (Hendershot et al. 2008). The soil pH was measured following the method of Rayment and Higginson (1992) using a pH electrode (Accumet pH meter model AB15, Fisher, Scientific, USA). Soil organic matter (SOM) was quantified by loss-on-ignition (Schulte et al. 1991). The soil moisture content ( $\theta$ ) was determined by the gravimetric method (ASTM 1988).

Parameter	Observe	d Value	Heavy Metal and Mineral concentrations			Allowable Threshol	
	(%, v	w/w)	$(mg \ kg^{-1})$			$(mg \ kg^{-1}) \ *$	
	BC	СР		BC	СР	BC	СР
Moisture TGA	3.88	4.38	Cd	<lod< td=""><td><lod< td=""><td>1.40</td><td>20.00</td></lod<></td></lod<>	<lod< td=""><td>1.40</td><td>20.00</td></lod<>	1.40	20.00
Ash TGA	19.29	64.43	Cr	29.80	19.91	64	1060
Volatile	18.19	29.09	Cu	<lod< td=""><td>44.22</td><td>63</td><td>757</td></lod<>	44.22	63	757
Fixed Carbon	62.53	6.47	Fe	706.71	8205.25	NA	NA
Carbon	70.40	18.80	Pb	<lod< td=""><td><lod< td=""><td>70</td><td>505</td></lod<></td></lod<>	<lod< td=""><td>70</td><td>505</td></lod<>	70	505
Hydrogen	2.20	1.83	Zn	33.11	90.01	200	1850
Nitrogen	1.07	1.28	Ν	5.12	36.81	NA	NA
Total Sulfur	0.53	0.16	Р	244.02	763.72	NA	NA
Oxygen	6.47	13.47	K	18201.05	4324.15	NA	NA
SSA $(m^2 g^{-1})$	8.5	2.05	Mg	520.23	1008.01	NA	NA
pH	9.61	7.87	Ca	750.09	4991.21	NA	NA
EC (mS cm <sup>-1</sup> )	4302.02	1226.61	Mn	40.02	40.15	NA	NA

Table 4.2: Properties of barley straw biochar (BC), and mixed green and table waste compost (CP)

TGA: thermogravimetric analysis; SSA: specific surface area; EC: electrical conductivity; NA: not available; \* *Based on* International Biochar Initiative allowable thresholds of heavy metals in biochar, and Guidelines for Compost Quality by Canadian Council of Ministers of the Environment (CCME, 2005) (mg kg<sup>-1</sup>).

# 4.3.3 Irrigation

The day before planting, each lysimeter was watered to field capacity using freshwater. After planting (day 0), each lysimeter was irrigated with wastewater every 10 days: eight times per season.

Category	Substance/compounds	Country	Concentration (mg L <sup>-1</sup> )	Reference
	Basic synthe	tic wastewater C	Constituents	
C Source	Na Acetate	NA	79.37	(Nopens et al. 2001)
	Milk powder	NA	116.19	
	Soy Oil	NA	29.02	
	Starch	NA	122	
	Yeast Extract	NA	52.24	
N Source	NH <sub>4</sub> Cl	NA	12.75	
	Peptone	NA	17.41	
	Urea	NA	91.74	
P Source	$Mg_3O_8P_2$	NA	29.02	
Minerals	CaCl <sub>2</sub>	NA	60	(LaPara et al. 2006)
	NaHCO <sub>3</sub>	NA	100	
Surfactant	Triton X-100	NA	*30	(Aboulhassan et al. 2006)
Heavy	Chromium (Cr)	India	2	(Ahmad et al. 2011)
Metals	Cadmium (Cd)	India	5	
	Lead (Pb)	India	16	
	Iron (Fe)(II)	India	120	
	Zinc (Zn)	India	3	
	Copper (Cu)(II)	India	8	
Hormones	Estrone: E1	S. Korea	*8.15 (20)	(Sim et al. 2011)
	Estradiol: E2	S. Korea	*0.634 (20)	
	Estriol: E3	S. Korea	*2.28 (20)	
	Ethinylestradiol: EE2	China	* 0.33 (20)	(Zhou et al. 2012)
	Progesterone	China	*0.90 (20)	(Huang et al. 2009)
PPCPs	Ibuprofen	Canada	*45	(Guerra et al. 2014)
	DEET	USA	*6.5	(Lietz and Meyer 2006)
	Caffeine	China	*6.6	(Sui et al. 2010)
	Carbamazepine	S. Korea	*21.6	(Sim et al. 2011)
	Diclofenac	India	*25.68	(Singh et al. 2014)
	Triclosan	UK	*21.9	(Sabaliunas et al. 2003)
	Oxytetracycline	China	*19.5	(Li et al. 2008)

# Table 4.3: Components and concentrations in synthetic wastewater

\*Concentrations in  $\mu$ g L<sup>-1</sup>, NA: not applicable, PPCPs: pharmaceutical and personal care products, numbers in () indicates the concentration used in this work.

Each wastewater irrigation consisted of 11.5 L of synthetic wastewater applied per lysimeter. The irrigation volume was determined based on the water requirements (500-700 mm) and growing season (120 days) of the potato crop. The make-up of the synthetic wastewater is given in **Table 4.3**. The organic contaminants and heavy metals concentrations were representative of a worst-case scenario wastewater.

#### 4.3.4 Plant Physiological Parameters

Relative chlorophyll content (SPAD) was estimated two days before each irrigation and five days after each irrigation, using a chlorophyll meter (SPAD-502 Plus; Konica Minolta). Plant photosynthetic activity, stomatal conductance, and transpiration rate were measured 5 days after each irrigation, using Li-Cor 6400 (LI-COR, Nebraska, USA). Crop vigor, quantified by reflectance [normalized difference vegetation index (NDVI)], was measured, five days after irrigation, using an active crop canopy sensor (Crop Circle ACS-470; Holland Scientific Inc., Nebraska, USA).

# 4.3.5 Plant Harvest

In both years, potatoes in each lysimeter were harvested 120 days after planting, as per local growing season recommendations for 'Russet Burbank' potatoes. Above-ground biomass was cut off at ground level with a knife, then separated into stems and leaves. The weight of the above-ground biomass, number of branches, shoot weight, and the height of the shoot were measured. The under-ground biomass was harvested, roots and tubers separated and weighed, and the yield components counted and graded (number of tubers, weight of tubers and graded tuber (50 mm) weight and numbers (Shiri-e-Janagard et al. 2009; USDA 1983).

# 4.3.6 Data Analysis

Physiological parameters were analyzed by considering the treatment and measurement time as factors. For soil properties, plant growth, and yield components, treatment was considered as the only factor, therefore the analyses were one-way Analysis of Variance. Each year was analysed

separately. Least significant difference test was used for a pair-wise comparison, and differences were considered significant when  $p \le 0.05$ . All analysis was performed using IBM SPSS® V.24 (Copyright © IBM Corp 2016 Armonk, NY).

# 4.4 Results

#### 4.4.1 Soil Physiochemical Properties

Our results indicated that the application of single or combined compost and biochar amendments  $(BC_1CP_0, BC_3CP_0, BC_0CP_{7.5}, BC_1CP_{7.5}, BC_3CP_{7.5})$  altered soil physicochemical properties, as compared with the non-amended control  $(BC_0CP_0)$ . The soil CEC, SOM, and pH were significantly increased by soil amendment with compost (**Table 4.4**).

**Table 4.4:** Effects of biochar, compost and biochar-compost mix on soil cation exchange capacity (CEC), soil organic matter (SOM), and pH.

Treatments	CEC (cmol(+) kg <sup>-1</sup> )		SOM	[ (%)	рН		
	Surface	0.10 m	Surface	0.10 m	Surface	0.10 m	
BC <sub>0</sub> CP <sub>0</sub>	1.78±0.29 <sup>b</sup>	2.62±1.24 <sup>c</sup>	2.79±0.64°	2.72±0.18 <sup>b</sup>	$5 \pm 0.10^{d}$	5.26±0.14 <sup>d</sup>	
$BC_1CP_0$	1.69±0.31 <sup>b</sup>	1.88±0.33°	2.89±0.37°	$3.07{\pm}0.56^{b}$	5.18±0.15 <sup>cd</sup>	$5\pm0.21^{d}$	
BC <sub>3</sub> CP <sub>0</sub>	1.94±0.44 <sup>b</sup>	4.12±1.34 <sup>bc</sup>	2.84±0.67°	2.90±0.31 <sup>b</sup>	5.33±0.14 <sup>bc</sup>	6.11±0.03°	
BC <sub>0</sub> CP <sub>7.5</sub>	$4.58 \pm 0.94^{a}$	7.39±0.93 <sup>ab</sup>	$3.19 \pm 0.70^{bc}$	$3.87{\pm}0.89^{ab}$	5.6±0.11ª	$6.43 \pm 0.32^{bc}$	
BC1CP7.5	$4.60 \pm 1.46^{a}$	5.54±0.29 <sup>b</sup>	$4.76\pm0.10^{b}$	$3.62\pm0.17^{ab}$	5.43±0.17 <sup>ab</sup>	6.5±0.14 <sup>b</sup>	
BC <sub>3</sub> CP <sub>7.5</sub>	5.73±2.74 <sup>a</sup>	$7.57{\pm}1.60^{a}$	6.77±1.91ª	4.89±1.49 <sup>a</sup>	5.66±0.11ª	7.13±0.15 <sup>a</sup>	

The different superscript lowercase letters in each column represent a significant difference at  $p \le 0.05$ ; values are mean  $\pm$  standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.

The CEC at the soil surface was higher ( $p \le 0.05$ ) in the BC<sub>3</sub>CP<sub>7.5</sub>, BC<sub>1</sub>CP<sub>7.5</sub>, and BC<sub>0</sub>CP<sub>7.5</sub> treatments, than in the BC<sub>3</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, and BC<sub>0</sub>CP<sub>0</sub> treatments. However, at the 0.10 m soil depth, the CEC was only significantly higher ( $p \le 0.05$ ) in the BC<sub>3</sub>CP<sub>7.5</sub> treatment than under other treatments, except for BC<sub>0</sub>CP<sub>7.5</sub>. No significant differences were observed between the soil CEC under the BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, and BC<sub>3</sub>CP<sub>0</sub> treatments. At both soil depths (surface and 0.10 m), SOM was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, or BC<sub>3</sub>CP<sub>0</sub>. There was no significant (p > 0.05) difference between BC<sub>1</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>0</sub> relative to the BC<sub>0</sub>CP<sub>0</sub> control at either depth. Similarly, at both depths, soil under the BC<sub>0</sub>CP<sub>7.5</sub>, and BC<sub>3</sub>CP<sub>7.5</sub> treatments showed a higher (p ≤ 0.05) pH than soils treated with BC<sub>1</sub>CP<sub>0</sub> or receiving no amendment (BC<sub>0</sub>CP<sub>0</sub>). Also, BC<sub>3</sub>CP<sub>7.5</sub> and BC<sub>1</sub>CP<sub>7.5</sub> showed higher (p ≤ 0.05) pH values than their compost-free counterparts BC<sub>3</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub>, at either depth. No significant difference was observed between BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> at either depth.



**Figure 4.2:** Moisture content of soil collected two days after irrigation one (Irrig1), four (Irrig4) and eight (Irrig8) in 2017 and 2018. The different letters on the bars in each column represent significant difference at  $p \le 0.05$ ; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.

In 2017, on 2 days after first irrigation, the  $\theta$  was higher (p  $\leq$  0.05) under BC<sub>3</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>0</sub> than under all other treatments (**Fig4.2**; 2 Days after irrigation four, the  $\theta$  for the BC<sub>3</sub>CP<sub>7.5</sub> was higher (p  $\leq$  0.05) than that under the control (BC<sub>0</sub>CP<sub>0</sub>). However, neither amendment influenced  $\theta$  on 2 days after irrigation eight. No amendment effects on  $\theta$  were observed in 2018 for 2 days after

irrigation four, and on 2 days after irrigation eight, when  $\theta$  under BC<sub>3</sub>CP<sub>7.5</sub> was higher than under BC<sub>3</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, or BC<sub>0</sub>CP<sub>0</sub>. A similar increase was also observed on 2 days after first irrigation, where  $\theta$  was higher under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>1</sub>CP<sub>0</sub>, BC<sub>3</sub>CP<sub>0</sub>, or BC<sub>0</sub>CP<sub>0</sub>.

# 4.4.2 Plant Growth Parameters

No amendment treatment affected plant growth parameters (plant height, no. of branches, shoot fresh weight or root fresh weight, **Fig 4.3**), relative to the  $BC_0CP_0$  control in either year. Plant height and shoot fresh weight were greater in 2018 compared with 2017. For example, the mean shoot weight for  $BC_0CP_0$  was 0.9 kg in 2017 and 1.45 kg in 2018, while for  $BC_3CP_{7.5}$  shoot weight was 0.9 kg in 2017 and 1.45 kg in 2018, while for  $BC_3CP_{7.5}$  shoot weight was 0.9 kg in 2017 and 1.31 kg in 2018.



**Figure 4.3:** Effect of biochar and/or compost amendments on potato (A) plant height, (B) potato number of branches, (C) potato root weight, and (D) shoot weight in 2017 and 2018. The different letters on the bars in each column represent significant difference at p < 0.05; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.

Similarly, mean shoot height for  $BC_0CP_0$  was 997 mm in 2017 and 1,212 mm in 2018, while for  $BC_3CP_{7.5}$  it was 943 mm in 2017 and 1061 mm in 2018. The increase in plant growth parameters during the second season can be attributed to a greater mean temperature in the summer of 2018 than 2017. Increased temperatures, up to a point, can facilitate plant uptake of nutrients to the aboveground biomass as a result of enhanced photosynthesis and faster evolving plant phenology.

# 4.4.3 Plant Physiological Parameters

The plant physiological parameters of SPAD, NDVI, transpiration rate, stomatal conductance, and photosynthesis showed no significant treatment effect (p > 0.05); however, there was a significant time effect ( $p \le 0.05$ ) in both years (**Fig. 4.4**), *i.e.*, SPAD readings declined with plant age. Another indicator for plant canopy health or vigor measured over the 2 years, the NDVI also showed no significant difference (p > 0.05) across treatments (**Fig. 4.5**), indicating that the treatments did not impact above-ground plant growth, in comparison to the control (BC<sub>0</sub>CP<sub>0</sub>). In 2017 NDVI ranged from 0.87 (Day 51) to 0.78 (Day 91), while in 2018, NDVI ranged from 0.79 (Day 55) to 0.85 (Day 95).

LICOR measurements of photosynthesis and transpiration rates, as well as stomatal conductance, were only taken in 2018 (**Fig. 4.6**). None of these parameters showed any significant single treatment or treatment interaction (treatment × time) effect. However, time had a significant effect ( $p \le 0.05$ ) on response. The photosynthetic rate ranged from a maximum of 11.7 µmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> (day 65) to a minimum of 5.4 µmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> (day 95). Transpiration rate ranged from a minimum of 0.59 mmol H<sub>2</sub>O m<sup>-2</sup> s<sup>-1</sup> (day 45) to a maximum of 3.9 mmol H<sub>2</sub>O m<sup>-2</sup> s<sup>-1</sup> (day 65). Stomatal conductance ranged from a maximum of 0.48 mol H<sub>2</sub>O m<sup>-2</sup> s<sup>-1</sup> (day 65) to a minimum of 0.074 mol H<sub>2</sub>O m<sup>-2</sup> s<sup>-1</sup> (day 95).



**Figure 4.4:** Effect of biochar, compost and biochar-compost mix on potato plant greenness readings (SPAD) in (A) 2017 and (B) 2018. The same letters on the bars in each column represent no significant difference at  $p \le 0.05$ ; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar

alone, BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.



**Figure 4.5:** Effect of biochar, compost and biochar-compost mix on normalized difference vegetation index (NDVI) readings on potato plants in (A) 2017 and (B) 2018. The same letters on the bars in each column represent no significant difference at  $p \le 0.05$ ; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.



**Figure 4.6:** Effect of biochar, compost and biochar-compost mix on (A) photosynthetic rate, (B) transpiration rate and (C) stomatal conductance of potato plants in 2018. The different letters on the bars in each column represent significant difference at  $p \le 0.05$ ; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.

# 4.4.4 Yield Components

Yield components for each treatment were compared to the BC<sub>0</sub>CP<sub>0</sub> control group (**Fig. 4.7**). The greatest mean tuber weight observed in both years was for BC<sub>3</sub>CP<sub>7.5</sub> at 1.58 kg in 2017 and 0.88 kg in 2018. Compared to the BC<sub>0</sub>CP<sub>0</sub> non-amended treatment, no significant differences (p > 0.05) were observed in either year for the compost treatments alone or in combination with biochar. Compared to 2017, mean potato tuber weight per plant in 2018 decreased by 28.3% in the BC<sub>0</sub>CP<sub>0</sub> treatment (0.88 kg in 2017 to 0.64 kg in 2018). The corresponding reductions under BC<sub>1</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>7.5</sub>, BC<sub>0</sub>CP<sub>7.5</sub>, and BC<sub>3</sub>CP<sub>7.5</sub> were 66, 61, 50, and 44%, respectively. Potato tuber weight did not reduce in the BC<sub>3</sub> (BC<sub>3</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>7.5</sub>) treatments in either year. No significant difference (p > 0.05) in the number of tubers per plant was observed between the amended treatments and the BC<sub>0</sub>CP<sub>0</sub> control in either year. The number of tubers that were not damaged and over 50 mm in size (*i.e.*, marketable potatoes) was not significantly affected (p > 0.05) by amendment treatments (compared with control BC<sub>0</sub>CP<sub>0</sub> or between treatments) in either year.



**Figure 4.7:** Effects of biochar, compost and biochar-compost mix on potato (A) Tuber weight, (B) number of tubers, and (C) tuber grading in 2017 and 2018. The different letters on the bars in each column represent significant difference at  $p \le 0.05$ ; Error bars are standard error of three replicates. BC<sub>0</sub>CP<sub>0</sub>: non-amended soil; BC<sub>1</sub>CP<sub>0</sub>: 1% biochar alone; BC<sub>3</sub>CP<sub>0</sub>: 3% biochar alone; BC<sub>0</sub>CP<sub>7.5</sub>: 7.5% compost alone; BC<sub>1</sub>CP<sub>7.5</sub>: 1% biochar and 7.5% compost; and BC<sub>3</sub>CP<sub>7.5</sub>: 3% biochar and 7.5% compost.
#### 4.5 Discussion

Biochar and biochar-compost mixes have previously been shown to improve soil properties (Agegnehu et al. 2017). This was also observed in the present study: amendment with compost and biochar-compost mixes significantly increased ( $p \le 0.05$ ) soil CEC, pH and SOM (**Table 4.4**).

As the compost amendment's mineral content exceeded that of biochar (**Table 4.2**), a significant  $(p \le 0.05)$  and greater increase in soil CEC, relative to non-amended soil, was found for the singly applied compost treatment than either singly-applied biochar treatments. Epstein et al. (1976) found that upon a soil's amendment with compost, the minerals it bears are released to the soil, thereby increasing exchangeable cations in the soil exchange complex. Under combined compost-biochar amendments, one would therefore expect that a greater rate of biochar application would result in a greater retention of compost-borne minerals within the compost, thereby increasing the soil CEC.

At corresponding levels of biochar amendment (BC<sub>0</sub>, BC<sub>1</sub>, BC<sub>3</sub>), wastewater irrigated soils amended with compost (CP<sub>7.5</sub>) showed greater SOM levels than those receiving no compost amendment (CP<sub>0</sub>). These observations that, under wastewater irrigation, a compost amendment enhances SOM, closely concurs with the results of Marofi et al. (2015). This effect is likely tied to the compost's high organic matter content (**Table 4.4**). However, an increased SOM can also be associated with soil amendments' rate of mineralization. As compost bears less fixed C (**Table 4.2**) and exhibits a lesser C/N ratio than biochar, compost would mineralize faster in soil (Bolan et al., 2012). Although soil amendment with biochar alone did not increase SOM, raising its application rate from 1% to 3% in compost treatments (CP<sub>7.5</sub>) did improve mineralization of organic matter, thereby increasing SOM levels (**Table 4.4**). Therefore, when co-amending soils with biochar and compost, an increase in the rate of biochar amendment may increase SOM.

Temperature (°C)	May	June	July	August	September	October
2017						
Max	17.5	23.2	24.8	24.2	23.2	18.4
Min	8.2	13.6	15.3	14.0	12.4	7.1
Mean	12.9	18.4	20.1	20.1	17.8	12.8
2018						
Max	21.4	23.7	29.2	27.4	22.5	10.2
Min	8.7	12.8	17.6	17.3	11.9	3.1
Mean	15.1	18.4	23.4	22.3	17.2	6.6

**Table 4.5:** Monthly mean daily minimum, maximum and mean temperature for Sainte-Anne-de-Bellevue, Quebec, for 2017 and 2018 (Environment Canada, 2021)

Overall, our results suggest that soil amendment with a combination of the higher percentage of biochar (3%) along with compost, may help stabilize and retain the organic matter contributed by the compost. In contrast, Agegnehu et al. (2015) found that a mixed amendment of compost and biochar had no more effect on SOC as an indicator of SOM than compost or biochar amendments alone. This disparity may reflect the different sources, rates and ratios of amendments used in the two studies.

The 2017 potato tuber yield stood within the range (0.90 to 2.12 kg per plant) reported by Bethke et al. (2014) for cv. 'Russet Burbank', cultivated in Canada, over three growing seasons. In 2018, the tuber yield declined for all treatments, except those amended with 3% biochar alone or in combination with compost (0.89 kg per plant). The differences in temperature between the growing seasons of 2017 (6 days with temperatures above 30°C) and 2018 (18 days with temperatures above 30°C) could have been the reason for lower yield in 2018 (**Table 4.5**). Indeed, high temperatures can affect both tuber initiation and growth by reducing the potato plant's CO<sub>2</sub> assimilation rate (Ku et al. 1977). At temperatures above 25°C, a greater portion of mass is partitioned towards above-ground biomass than towards tubers (Van Dam et al. 1996), while above 30°C, tuber growth rates decline substantially (Burton 1972), leaving tubers unformed or severely delayed in development (Mendoza and Estrada 1979). Accordingly, the hypothesis that high temperatures impeded potato tuber development in 2018 is strongly supported. Although not applicable in the present study, disease and low seed quality may also affect potato yield (Kooman and Haverkort 1995; Kooman 1995).

In both years, the improved soil CEC and SOM could explain the improved tuber yield observed in the soils amended with compost and biochar-compost mixes. Increased CEC and SOM are known to increase nutrient availability to plants, including potatoes (Porter et al. 1999). In 2017, the greater soil CEC and SOM under the compost and biochar mix (BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub>) treatments led to significantly improved tuber yields, compared to the BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, and BC<sub>3</sub>CP<sub>0</sub> treatments. In 2018, tuber yields under BC<sub>3</sub>CP<sub>7.5</sub> were greater than those under the BC<sub>1</sub>CP<sub>0</sub> treatment, with the only other significant difference being between BC<sub>1</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>0</sub> treatments. On the basis of both years' results, the treatment combination of BC<sub>3</sub>CP<sub>7.5</sub> improved yield the most. Our results are consistent with several other studies, where crop yield increased with biochar amendment (Barrow 2012; Blackwell et al. 2015; Chan et al. 2008) but was in contrast with the decrease in yield observed by Deenik et al. (2010).

The improvement of soil properties by biochar and biochar-compost amendment explains, to a large extent, the improved plant growth conditions observed in both years for the biochar treatments. Biochar amendment in 2017 had a significant positive effect on potato tuber yield, compared to the non-amended control ( $BC_0CP_0$ ), while, in 2018, the tuber yield was significantly greater in the  $BC_3CP_0$  treatment than in either the  $BC_1CP_0$  or  $BC_0CP_0$  treatment. Therefore, we interpret this as showing that the impact of biochar amendment on plant yield may increase over time as the biochar gets conditioned (Wang et al. 2016b). Both SPAD and NDVI values were consistent with those in the literature (Shamal and Weatherhead 2014), although they showed no significant response to amendment treatments. This lack of amendment treatment effect parallels the results of Nzediegwu et al. (2019b) and may be associated with several factors, including the quality of irrigation water (Chartzoulakis and Klapaki 2000; Savvas et al. 2007) and/or water deficit (Dorji et al. 2005; Katerji et al. 1993), which adversely impact NDVI. As plant tolerance to water deficits in the root zone is limited, such deficits can negatively affect canopy biomass, thereby lowering the NDVI value, which in such a case is representative of lower crop production and health (De Pascale et al. 2003). Patil et al. (2014) reported a similar impact of wastewater *vs.* freshwater on NDVI when used for irrigation.

While significant differences in growth parameters were noted when cannabis (*Cannabis sativa* L.) plants were grown in a biochar-amended (*vs.* non-amended) soil (Chandra et al. 2008; Hussain et al. 2017), the same treatments applied to potato plants in the present study did not result in any significant difference in growth parameters, likely because of the difference in crops. Potatoes, being a tuber crop, may respond differently to changes in soil conditions imposed by soil amendments.

Overall, potato tuber yield reflected changes in soil properties, but the crop's above-ground growth parameters (*e.g.*, SPAD) did not. The decline in SPAD parameter values during the potato plant's growth and development (**Fig. 4.4**) reflect potato plants' different nutrient requirements at different physiological stages. Higher SPAD values between days 44 to 57, compared to those recorded at the end of growing season (**Fig. 4.4**), were likely representative of the greater nutrient accumulation into biomass during the vegetative phase than during the maturation stages (Nzediegwu et al. 2019b).

The similarity of potato yields achieved with wastewater irrigation in the present study and under freshwater irrigation (e.g., Bethke et al. 2014) indicates that wastewater had little or any

negative impacts on potato yield, thus highlighting the viability of using wastewater for crop production. Under the present study's wastewater irrigation regime, detectable levels of heavy metals were found in both the skin and flesh of potato tubers, as well as in potato roots and above-ground biomass, and this across all amendment combinations and in the non-amended control. However, heavy metal concentrations were significantly lower ( $p \le 0.05$ ) in the compost and biochar amended treatments as compared to the control. The potatoes produced under the present treatment combinations would likely be safe for consumption based on their having hazard quotients (Sharma et al., 2016) inferior to 1.0 for heavy metals such as Cu, Fe, and Pb.

#### 4.6 Conclusions

A two-year field lysimeter study was carried out to investigate the use of biochar and compost soil amendments in potatoes grown under wastewater irrigation. Amending a sandy soil with biochar, compost or biochar-compost mix significantly improved soil physicochemical properties (*e.g.*, cation exchange capacity, soil organic matter and pH), and potato yield depending on biochar application rate and biochar-compost mixing ratio. The change in soil physicochemical properties apparently led to improved nutrient uptake and greater yield. In two consecutive years, potato yield was greater under mixed biochar-compost soil amendments, than under biochar or compost amendments applied singly. However, it is recommended to conduct such studies for longer periods to draw more concrete conclusions as to the potential benefits or constraints accruing from such amendments.

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#### **Connecting Statement to Chapter 5**

In the literature review (Chapter 2), the fate and transport of PPCPs a group of emerging organic environmental contaminants, was discussed, and it was noted that additional research was needed to establish the influence on the mobility of soil-borne PPCPs of soil parameters (*e.g.*, pH, TOC, DOC and organic matter content) and the PPCPs' chemical properties (i.e., log K<sub>ow</sub>, pK<sub>a</sub>). In the experiments described in Chapter 3, we studied the fate and plant uptake of inorganic contaminants, while in the experiments described in Chapter 5, we studied the influence that soil amendments such as biochar and compost, individually or in concert, on the PPCPs' mobility in soil.

The study described in Chapter 5 represents the first attempt to evaluate the complex interplay between pharmaceutical chemical properties and soil chemical properties and how these govern potential exposure scenarios given their soil mobility. While more work is required to investigate the relationship between the PPCPs' chemical properties and their uptake by plants, the present study represents a first important step in understanding the fate of pharmaceuticals and personal care compounds in soil layers, a critical element in understanding environmental risk.

The following manuscript (Chapter 5) is being prepared for submission to the *Journal of Hazardous Materials*. The manuscript is co-authored by Prof. Shiv Prasher, research supervisor, Prof. Stéphane Bayen, research Co-supervisor, and Dr. Lan Liu in the Department of Food Science, McGill University. The original draft has been modified to ensure consistency with the thesis format, and the cited references are listed in the reference section (Chapter 10).

# 5 Chapter 5: Fate and transport of PPCPs in soil-plant system in the presence of sorbent materials

#### 5.1 Abstract

The need to produce more food for the world's growing human population had led to a greater demand for fresh water for irrigation. To meet this demand, wastewater irrigation has become a common practice in many countries. However, the presence of emerging organic contaminants [e.g., pharmaceuticals and personal care products (PPCPs)] in wastewater could represent a major risk, as these contaminants may be harmful to the environment and pose a risk to human health. There is an urgent need to understand how soil amendments can help reduce risks of emerging contaminants applied to agroecosystems through irrigation water. A two-year field lysimeter study (2017/18) investigated the effects of soil amendments created from organic wastes (e.g., green and table waste compost, barley straw biochar) on the transport of selected irrigation wastewater borne PPCPs (e.g., caffeine, carbamazepine, DEET, diclofenac, and triclosan) in soil. Biochar alone or in combination with compost was incorporated into the top layer (0-0.10 m depth) of a sandy soil. Six thrice-replicated treatments were tested in a completely randomized design (CRD): (i) nonamended soil BC<sub>0</sub>CP<sub>0</sub> (WW) control, (*ii*) 1% biochar (w/w) BC<sub>1</sub>CP<sub>0</sub>, (*iii*) 3% biochar BC<sub>3</sub>CP<sub>0</sub>, (*iv*) 7.5% compost BC<sub>0</sub>CP<sub>7.5</sub>, (v) 1% biochar and 7.5% compost BC<sub>1</sub>CP<sub>7.5</sub>, and (vi) 3% biochar and 7.5% compost BC<sub>3</sub>CP<sub>7.5</sub>. The soil mobility of PPCPs, provided a wider understanding of the relationship between PPCPs' properties (e.g., water solubility, octanol-water partition coefficient, acid dissociation constant) and soil mobility. In general, the high application rate of biochar 3% alone on in combination with compost reduced ( $p \le 0.05$ ) the soil mobility of PPCPs compounds (CAF, CBZ and DEET). The results are discussed in the context of the physicochemical parameters (e.g., water solubility, octanol-water partition coefficient, and acid dissociation

constants) of organic contaminants and surface morphology of the soil amendments and their potential interaction with the PPCPs compounds.

**Keywords:** Wastewater irrigation, PPCPs, Soil amendments, Soil properties, *Solanum tuberosum* L, Sandy soil.

# 5.2 Introduction

Agriculture is currently the largest worldwide consumer of water, and its demands are constantly increasing. Showing a high growth potential (Hettiarachchi and Ardakanian, 2016) and already practiced on over  $0.20 \times 10^6$  km<sup>2</sup> of arable lands around the world, wastewater irrigation has proven a logical alternative in several developing countries because as it can fulfill much of the crop's nutrient requirements and reduce/eliminate the need for fertilizers. Moreover, its relatively steady supply and low cost encourage its continued use.

Besides having the potential to increase agricultural food production and promote freshwater conservation, wastewater irrigation can also limit the harmful practice of openly discharging untreated wastewater into the environment as commonly occurs in developing regions (Qadir et al., 2010). However, to prevent contamination of the surrounding environment, wastewater must be treated to some degree before its use in irrigation. Wastewater can potentially contain a combination of inorganic and organic contaminants including hormones and PPCPs. Some of those wastewater contaminants may be endocrine disruptors, along with other carcinogenic, mutagenic and teratogenic compounds (Tucker and Carson, 1985; Xing et al., 2007), toxic to humans (Fairchild et al., 1998).

Pharmaceuticals are defined as prescription, over the counter or veterinary therapeutic drugs used to prevent or treat human and animal diseases. Personal care products are used mainly

to improve the quality of daily life (Boxall et al., 2012). Pharmaceuticals can be ranked according to persistence, bioaccumulation, and toxicity. According to Howard and Muir (2011), carbamazepine, ibuprofen, and diclofenac are amongst the top-selling pharmaceutical compounds.

As such, wastewater and biosolids contain these "emerging contaminants". When wastewater and biosolids are applied to agricultural lands, PPCPS may enter agricultural soils and potentially contaminate water bodies and food crops (Wu et al., 2015). The fate of organic contaminants and their uptake from soils into plants can be influenced by several factors including the contaminants' physiochemical properties (*e.g.*, water solubility, octanol-water partition coefficient and acid dissociation constant) (Wu et al., 2015), environmental characteristics (*e.g.*, soil type, temperature, and soil moisture content) and plant characteristics (*e.g.*, root system, leaf shape and size and lipid content) (Colon and Toor, 2016). Likewise, contaminant uptake can vary depending on the plant species. For example, contaminant uptake from soil is likelier in root vegetables (*e.g.*, potatoes, carrots) than stem-borne fruits (*e.g.*, tomatoes, apples), since root crops are in closer contact with soil and water than fruit part (Trapp and Legind, 2011). Therefore, there is an urgent need to develop cost-effective, efficient, simple and easy-to-use techniques to control the transport and translocation of contaminants through wastewater irrigation.

Biochar, produced from the pyrolysis of organic waste materials has shown benefits in water treatment (Abit et al., 2012; Kookana et al., 2011). Its large surface area and pore volume (Ding et al., 2016) favors the sorption of heavy metals (Ding et al., 2016; Kumar et al., 2011). Moreover, laboratory and field-scale experiments have shown that biochar can reduce the movement of organic and inorganic contaminants in soil and water systems (Ahmad et al., 2014; Cabrera et al., 2014; Chen and Chen, 2009; Mohanty and Boehm, 2014). Biochar may also reduce translocation of organic contaminants to crops (Hurtado et al., 2017). Soil amendments, including

biochar, can immobilize many PPCPs and other organic compounds, including persistent organic pollutants (POPs), polychlorinated biphenyl (PCBs), and polycyclic aromatic hydrocarbon (PAHs) (Zhang et al., 2013b). They may also reduce their bioavailability to plants (Williams et al., 2015). Compost has also shown the ability to immobilize inorganic and organic contaminants in polluted soil and reduce their bioavailability (Beesley et al., 2010; Hurtado et al., 2017). Compost can increase the soil's cation exchange capacity (CEC) and pH, improve its buffering capacity, degrade and immobilize persistent organic pollutants, and mineralize inorganic pollutants (Fischer and Glaser, 2012). Moreover, compost can contribute to the remediation of many natural and anthropogenic organic pollutants (Kästner and Miltner, 2016). Compost can act as a biostimulation and bio-augmentation agent, as it provides a diversity of microorganism, nutrients for their growth, and organic matter that acts as a stimulant (Kästner and Miltner, 2016). Thus, compost could help remediate organic contaminants by assisting in their degradation (Kästner and Miltner, 2016). However, it has also been posited that organic matter in soil can suppress the sorption of organic contaminants onto biochar through competition for micropore space (Zhang et al., 2013b).

From the literature, it is evident that PPCPs in wastewater would either enter in water bodies or soil. Some PPCPs can also translocate into crops grown in contaminated soil or irrigated with wastewater. Our study focused on determining how biochar (at two application rates, 1% and 3% w/w) and compost (at a single rate, 7.5% w/w), singly or in combination, would affect the physiochemical properties of a sandy soil and how this would, in turn, influence the fate of PPCPs in the soil and their mobility. The results of such a study would provide a greater insight into the relationships between soil properties and soil mobility of contaminants from wastewater irrigation. To better understand any difference in the potential effects of treatments in the soil-plant system, the research focused on five PPCPs, covering a range of physicochemical characteristics and range of medical uses.

#### 5.3 Methods and Materials

#### 5.3.1 Chemicals and Standards

HPLC-grade solvents [water, acetone, methanol, acetonitrile, ethyl acetate and MTBE (methyl tert-butyl ether)], as well as LC/MS-grade formic acid, were all purchased from Fisher Chemicals (Waltham, MA, USA). Pharmaceutical and personal care product (PPCPs) analytical standards for caffeine (CAF; purity  $\geq$  99.0 %), carbamazepine (CBZ; purity  $\geq$  98%), DEET (DEET; purity  $\geq$  97.0-103.0%), diclofenac (DCF; purity  $\geq$  98.0%), and triclosan (TCS; purity  $\geq$  97.0-103.0 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The physiochemical properties and the chemical structure of the PPCPs are summarized in **Table 5.1**. Labelled internal standards, including carbamazepine-d<sub>10</sub> (99.5% purity), caffeine-d<sub>3</sub> (99.7% purity), diclofenac-d<sub>4</sub> (98.1% purity), triclosan-d<sub>3</sub> (97.2% purity), 17α-ethynylestradiol-d<sub>4</sub> (98.8% purity) and N, N-Diethyl-3-methyl-d<sub>4</sub> (98.8% purity), were purchased from C/D/N Isotopes (Pointe-Claire, Canada).

#### 5.3.2 Field Experimental Setup

A 2-year (2017, 2018) study was conducted using field lysimeters located at the Macdonald Campus of McGill University, Sainte-Anne-de-Bellevue, QC, Canada ( $45^{\circ}24'48.6"$  N latitude and  $73^{\circ}56'28.1"$  W longitude). In the spring of 2017, field lysimeters (1.0 m height × 0.45 m I.D) were filled with a sandy soil obtained on-site. Across the intervening winter, the experimental units were protected with plastic bags to prevent freshwater from rainfall or snow entering the lysimeter over the winter months. A detailed description of the soil is provided in (**Table 4.1**).

Compounds CAS	MW (g/mol)	Structure	рКа	Log Kow	Water solubility (mg/L)	Log Koc
Caffeine (CAF) 58-08-2	194.19	$H_{3}C \underset{O}{\overset{O}{\underset{K}}} \underset{O}{\overset{O}{\underset{K}}} \underset{N}{\overset{O}{\underset{K}}} \underset{N}{\overset{O}{\underset{K}}} \underset{N}{\overset{C}{\underset{K}}} \underset{N}{\overset{C}{\underset{K}}} \underset{N}{\overset{C}{\underset{K}}}$	0.614	-0.07	2632	0.98
Carbamazepine (CBZ) 298-46-4	236.28		15.4	2.45	17.66	2.22
DEET 134-62-3	191.27	O N CH <sub>3</sub> CH <sub>3</sub>	0.91	2.18	666	1.85
Diclofenac- sodium (DCF) 15307-79-6	318.13		4.15	0. 7	2425	0.5
Triclosan (TCS) 3380-34-5	289.5		7.9	4.66	4.621	3.92

**Table 5.1:** Physicochemical properties for selected study compounds

EPI Suite software (US EPA) were used to estimate physical-chemical properties of the target PPCPs.

Five treatments and one wastewater (WW) control, replicated three times, were tested in a completely randomized design (CRD): (*i*) non-amended soil (WW control) ( $BC_0CP_0$ ); (*ii*) 1% biochar alone, ( $BC_1CP_0$ ); (*iii*) 3% biochar alone, ( $BC_3CP_0$ ); (*iv*) 7.5% compost alone, ( $BC_0CP_{7.5}$ ); (*v*) 1% biochar and 7.5% compost, ( $BC_1CP_{7.5}$ ); and (*vi*) 3% biochar and 7.5% compost, ( $BC_3CP_{7.5}$ ).

Based on the allocated treatment, biochar and/or compost were thoroughly mixed into the soil, ensuring homogeneity in the upper 0.10 m layer of the lysimeter soil at the onset of the

experiments. Compost was added to the soil at a rate of 7.5% (w/w), while biochar was added at rates of 1% or 3% (w/w). Each lysimeter was irrigated with 11.5 L of synthetic wastewater every ten days. The irrigation volume was determined based on the water requirements (500-700 mm) and the growing season (120 days) of the potato crop. The concentrations of various contaminants in synthetic wastewater have been documented elsewhere (**Table 4.3**) and were based on published literature. The compost and biochar remained in the lysimeters after harvest and were present at the onset of the second-year experiment.

# 5.3.3 Physicochemical and Morphology Characterization of Biochar and Compost

The barley straw biochar and compost characterization are given in **Table 4.2**. The specific surface area (SSA) was determined using the BET (Brunauer-Emmet-Teller) method, whereby nitrogen adsorption was used to find the specific surface area of the biochar and compost (Amziane and Collet, 2017; Jiang et al., 2012). The samples were analyzed under Scanning electron microscopy (FEI Inspect F50 FE-SEM). Small samples of biochar and compost samples were coated with platinum using a Sputter Coater (Leica Microsystems EM ACE600). The coated samples were then examined under an SEM (FEI Inspect F50 FE-SEM) at various magnifications based on procedures, outlined by George et al. (2005). The functional groups of biochar and compost samples were analyzed using Fourier-transform infrared spectroscopy (FTIR) (Agilent 5500a FTIR, Agilent Technologies USA), following the pellet method. Samples (1 mg) of dried biochar and compost were ground and mixed with 100 mg KBr (FT-IR grade,  $\geq$  99%; Sigma Aldrich) and pressed into pellets. The spectra were investigated in the range of 400–4000 cm<sup>-1</sup> at a 4 cm<sup>-1</sup> resolution using an FT-IR (Jin et al., 2016).

#### 5.3.4 Soil Physicochemical Parameters

At the end of the second season, soil samples were collected from each lysimeter, both at the surface and at a depth of 0.10 m, to measure the soil pH. Soil samples (10 g d.w.) were mixed with water (20 mL) and stirred for 30 minutes (Rayment and Higginson, 1992). The pH was measured with an electrode (Accumet pH meter model AB15, Fisher, Scientific, USA). Total organic carbon (TOC) was determined using a NC Soil Analyzer (Thermo Finnigan Flash EA-1112, Thermo Fisher Scientific Inc., MA, USA). Soil dissolved organic carbon was determined in soil samples using a TOC analyzer (Sievers InnovOx Laboratory).

#### 5.3.5 Soil Sampling and Analysis

To allow contaminants and the sorbent materials (biochar and compost) to equilibrate after an irrigation event, soil samples from each lysimeter were collected from surface soil (0-0.02 m) and three depths (0.10, 0.30 and 0.60 m), two days after each irrigation. At each depth, four holes (10 mm diameter) were drilled to collect soil samples along the depth of the column. Soil samples were stored in aluminum foil pouches at -20°C.

The extraction of PPCPs (DEET, triclosan, diclofenac, caffeine, and carbamazepine) from the soil samples followed a method, modified from that of Dodgen and Zheng (2016). In brief, 1 g (d.w.) of each soil sample was weighed and transferred to a 50 mL polypropylene centrifuge tube, and the sample was spiked with mass-labelled contaminant compounds. Soil extraction with acetone: methanol [50:50 (v/v)] was repeated three times (20, 15 and 15 mL, respectively). The 50 mL sample solutions were then vortexed for 5 minutes, sonicated for 20 min at room temperature and then centrifuged for 15 min at 4000 rpm. The supernatant was collected after each subsequent extraction step. The 50 mL extracts were evaporated to a final volume of 0.5 mL under nitrogen in a 40°C water bath. Then, 29.5 mL of ultrapure water (pH 2) was added to bring the volume to 30 ml. All PPCPs compounds were extracted using solid-phase extraction (SPE) techniques, employing Oasis cartridges (Oasis HLB, 60 mg, 3cc) purchased from Waters (Milford, MA, USA). Cartridges were conditioned by eluting with 10 mL of methanol, 6 mL water, followed by 6 mL of reagent water at pH 2.0  $\pm$  0.5. Samples were loaded into the cartridges at a flow rate of 5 mL min<sup>1</sup>. The cartridges were washed with 20 mL of reagent water and then dried under vacuum for 30 minutes. Analytes were eluted from the cartridges using 7 mL of acetone:methanol (50:50 v/v)) and 7 mL of ethyl acetate:methanol (90:10 v/v). The 14 mL extracts were allowed to dry gently under nitrogen gas in a 40°C water bath and reconstituted with 1 mL acetonitrile:water (50:50 v/v)). The 1 mL reconstituted extract was passed through a 0.22 µm syringe-driven filter into 1.5 mL amber colored HPLC vials and stored at -20°C for analysis.

## 5.3.6 Instrumental Analysis and Quantification

Contaminants in soil and plant tissues samples were analyzed using an Agilent 1290 Infinity II LC system (Agilent technologies, Santa Clara, USA) coupled to a 6545 quadrupole Time-of-Flight Mass Spectrometer (Agilent Technologies, Santa Clara, USA) on two runs corresponding to positive (ESI+) and negative (ESI-) electrospray ionization modes. The (ESI+) was run for caffeine, carbamazepine, and DEET, while (ESI-) were run for diclofenac, and triclosan. All targeted PPCPs were separated on a C18 column (RRHD Eclipse Plus C18, 2.1x100mm, 1.8u, Agilent with Plus UHPLC Guard, Eclipse). The mobile phase consisted of water (solvent A) and acetonitrile (solvent B), and the flow rate was set at 0.2 mL min<sup>-1</sup>.

#### 5.3.7 Quality Control/Quality Assurance (QA/QC)

Mass labelled standards were used as internal standards, an approach known to correct for matrix effects. Concentrations were obtained using the response factor (RF) for each set of analyte/internal standard according to Eq.1. Recoveries for each compound were calculated

according to Eq.2. Uncontaminated sandy soil was included as blank controls. Laboratory blanks, three spiked matrices (recovery) and solvent blanks (methanol/water, 1:1 v/v) were included with each sample batch of 10 samples. The validation process of Dodgen and Zheng (2016) was performed using a blank matrix and known amounts of mass-labelled and native compounds. Six internal standards were used to evaluate the accuracy of the method for quantifying PPCPs and validate the extraction method: Spiking with labelled compounds was based on the known concentration of the target analytes (100 ng/L). The limit of detection (LOD) and the limit of quantification (LOQ) were assessed from procedural blanks as signal-to-noise (S/N) ratios of 3 and 10, respectively.

$$RF = 100 \times \frac{\frac{Peak Area Analyte}{Concentration Analyte}}{\frac{Peak Area IS}{Concentration IS}}$$
(1)

$$Recovery \% = 100 \times \frac{Measured Concentration}{Reference Concentration}$$
(2)

#### 5.3.8 Data Analysis

Soil physicochemical properties were analyzed using one-way Analysis of Variance (ANOVA), considering the treatment as the only factor. The PPCPs concentrations in soil were analyzed as a repeated-measures ANOVA under different treatments at different depths at different times. Statistical tests were performed using Proc GLM in SAS 9.4 (SAS Institute Inc., Cary, NC). The level of significance for all comparisons was 95% ( $p \le 0.05$ ).

## 5.4 Results

#### 5.4.1 Characterization of Biochar and Compost (SSA, SEM, and FT-IR)

The surface morphologies of barley straw biochar and compost were characterized using SSA, SEM, and FTIR. A detailed description of the biochar and compost used in this study is given in **Table 5.2**. The compost's SSA was  $(2.05 \text{ m}^2 \text{ g}^{-1})$ , lower than that of biochar  $(8.5 \text{ m}^2 \text{ g}^{-1})$ . The SEM imaging of the biochar and compost (Figure 5.1) shows four magnifications for biochar: (A) ×500, (B)  $\times 1000$ , (C)  $\times 5000$ , and (D)  $\times 10000$ , and two magnifications for the compost (E)  $\times 500$ , and (F) ×5000. The surface morphology and porous structures were clearly different between the two soil amendments. The SEM pictures confirmed the BET results that were obtained for each of the samples. Compost's surface roughness was clearly less than that of the biochar. Figure 5.2 shows the FTIR spectra of biochar and compost. The FTIR spectrum of biochar showed four peaks (broad peak 2854.71-2887.97 cm<sup>-1</sup> assigned to CH<sub>3</sub>, 2923.16 cm<sup>-1</sup> assigned to CH<sub>2</sub>, 1599.37 cm<sup>-1</sup> assigned to aromatic rings, C=C or C-C, and a peak at 1385.04 cm<sup>-1</sup> assigned to C=C) that are considered hydrophobic groups. Two further peaks (broad peak 3228.51-3581.54 cm<sup>-1</sup> assigned to O-H group and peak at 1046.26 cm<sup>-1</sup> assigned to C-O-C) are considered hydrophilic groups. In contrast, compost showed only two peaks at 2922.06 cm<sup>-1</sup> assigned to CH<sub>2</sub> and 1407.86 cm<sup>-1</sup> assigned to C=C groups which are hydrophobic groups, and four peaks at 3337.20 assigned as OH group, 1665.07 cm<sup>-1</sup> assigned as C=O carboxylic acid, 1623.62 cm<sup>-1</sup> assigned as C=O and 1032.22 cm<sup>-1</sup> assigned as C-O-C which are considered as hydrophilic group. Therefore, the findings suggests that biochar is more hydrophobic than compost (Table 5.2).



**Figure 5.1:** Scanning electron microscopy of biochar at four magnifications: (A)  $\times$ 500, (B)  $\times$ 1000, (C)  $\times$ 5000, and (D)  $\times$ 10000, and two magnifications for the compost (E)  $\times$ 500, and (F)  $\times$ 5000.



Figure 5.2: FTIR spectra of biochar and compost.

Spectral assignment	Peak Positions (cm <sup>-1</sup> )	Reference	Biochar	Compost
Hydrophobic functional groups				
-CH <sub>2</sub>	2925-2940	Uchimiya et al., 2010	2923.16	2922.08
-CH <sub>3</sub>	2850-2904	Uchimiya et al., 2010	2854.71-2887.97	
Aromatic ring	1580-1600	Chu et al., 2019	1599.37	
C-C	1580-1600	Chu et al., 2019	1599.37	
C=C	1450-1600	Chu et al., 2019	1599.37	
C=C	1380-1450	Zhang et al., 2017	1385.04	1407.86
Hydrophilic functional groups				
O-H (hydroxylic –OH)	3200-3600	Keiluweit et al. 2010	3337.13	3337.20
O=C carboxylic acid	1650-1740	Chu et al., 2019		1665.07
O=C	1610-1650	Uchimiya et al., 2010		1623.62
C-O-C	1047-1057	Uchimiya et al., 2010	1046.26	1032.22

**Table 5.2:** Major absorption peaks in the FT-IR spectra of biochar and compost.

#### 5.4.2 Effects of Biochar and Compost on Soil Properties (TOC, DOC, and pH)

The BC<sub>3</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>7.5</sub> treatments showed the greatest ( $p \le 0.05$ ) TOC percentage at 2.03% and 1.83%, respectively. However, the TOC of BC<sub>3</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>7.5</sub> were only significantly different from the BC<sub>0</sub>CP<sub>0</sub> treatment (TOC of 1.08 %) (**Table 5.3**).

At the soil surface, significant differences in DOC were observed between BC<sub>0</sub>CP<sub>7.5</sub>, BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub> treatments at 27.31 mg/kg, 23.35 mg/kg and 18.33 mg/kg, respectively; however, there were no significant differences between the BC<sub>0</sub>CP<sub>0</sub> (13.17 mg/kg), BC<sub>1</sub>CP<sub>0</sub> (11.62 mg/kg) and BC<sub>3</sub>CP<sub>0</sub> (13.38 mg/kg) treatments, though these treatments had significantly lower ( $p \le 0.05$ ) DOC than the treatments amended with compost. At 0.10 m soil depth, no significant differences were observed in the DOC level of the BC<sub>0</sub>CP<sub>7.5</sub> (24.10 mg/kg), BC<sub>1</sub>CP<sub>7.5</sub> (24.9 mg/kg) and BC<sub>3</sub>CP<sub>7.5</sub> (28.43 mg/kg), treatments, though these treatments contained significantly greater ( $p \le 0.05$ ) DOC than the BC<sub>0</sub>CP<sub>0</sub> (12.61 mg/kg) and BC<sub>1</sub>CP<sub>0</sub> (11.68 mg/kg) treatments. Moreover, the BC<sub>3</sub>CP<sub>0</sub> treatment, with a DOC of 19.85 mg/kg, did not differ significantly in DOC level from any other treatment. The **pH** at the surface soil was higher in treatments having received a compost amendment. The pH of the BC<sub>0</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub> treatments were not significantly different from that of the BC<sub>1</sub>CP<sub>7.5</sub> treatment but were significantly different from that of other treatments. At a depth of 0.10 m the pH of the BC<sub>3</sub>CP<sub>1</sub> and BC<sub>3</sub>CP<sub>7.5</sub> treatments were significantly higher ( $p \le 0.05$ ) than all other treatment not having received a compost amendment. The pH values of both BC<sub>0</sub>CP<sub>0</sub> and BC<sub>1</sub>CP<sub>0</sub> were significantly lower ( $p \le 0.05$ ) than those of other treatments.

**Table 5.3:** Effects of biochar, compost, and biochar-compost mix on total organic carbon (TOC), dissolved organic carbon (DOC), and pH

Treatments	TOC (%)	DOC (	(mg/kg)	p	pH		
		0 cm	10 cm	0 cm	10 cm		
BC <sub>0</sub> CP <sub>0</sub>	1.08±0.06 <sup>b</sup>	$13.17 \pm 0.85^{d}$	12.61±0.75 <sup>b</sup>	$5.01 \pm 0.10^{d}$	$5.26 \pm 0.14^{d}$		
$BC_1CP_0$	1.33±0.20 <sup>ab</sup>	$11.62 \pm 1.18^{d}$	$11.68 \pm 3.27^{b}$	5.18±0.15 <sup>cd</sup>	5.02±0.21 <sup>d</sup>		
$BC_3CP_0$	2.03±0.69 <sup>a</sup>	$13.38 \pm 1.67^{d}$	19.85±0.20 <sup>ab</sup>	5.33±0.14 <sup>bc</sup>	6.11±0.03°		
BC <sub>0</sub> CP <sub>7.5</sub>	$1.69 \pm 0.47^{ab}$	27.31±1.06 <sup>a</sup>	24.10±11.36 <sup>a</sup>	5.61±0.11 <sup>a</sup>	6.43±0.32bc		
BC1CP7.5	$1.68 \pm 0.29^{ab}$	23.35±2.69 <sup>b</sup>	24.90±2.45ª	5.43±0.17 <sup>ab</sup>	$6.50\pm0.14^{b}$		
BC <sub>3</sub> CP <sub>7.5</sub>	1.83±0.40 <sup>a</sup>	18.33±1.75°	28.43±8.03ª	5.66±0.11 <sup>a</sup>	$7.13\pm0.15^{a}$		

The different superscript lowercase letters in each column represent a significant difference at  $p \le 0.05$ ; values are mean  $\pm$  standard division of three replicates.

#### 5.4.3 Effect of Soil Amendments on PPCPs Mobility in Soil

The concentrations of PPCPs (CAF, CBZ, DCF, DEET and TCS) were evaluated at different soil depths (surface soil, 0.10 and 0.30 m) in both years of the experiment. Across all treatments, and with the exception of CBZ and DEET, no PPCPs were detected in soil samples collected at a depth of 0.30 m in the last sampling day in both years. Overall, CBZ and DEET concentrations were substantial in the upper soil layer and gradually decreased with depth until no difference could be observed between soil depths. In year-2, DCF was shown to have been transported to a depth of 0.10 m; however CAF was not detected at that depth or at a depth of 0.30 m in either year. A similar pattern of greater concentration in the topsoil layer was obtained from the TCS measurements.

In both years of the experiment, the concentration of PPCPs in soil samples from different depths (surface, 0.10 and 0.30 m), five treatments and one WW control, and different sampling dates (Day-41, Day-71, Day-91, and Day-111) were measured. Those concentrations measured at the soil surface are shown in **Figure 5.3**, while the repeated measures analysis is presented in **(Table 5.4).** The CBZ and DEET concentrations at a 0.10 m depth are presented in **Table 5.5**.

**Table 5.4:** Summary of fixed effects for surface soil PPCPs concentration from repeated measures (Time) analysis.

	Year-1				Year-2					
Effects	CAF	CBZ	DCF	DEET	TCS	CAF	CBZ	DCF	DEET	TCS
Treatment	ns	*	ns	*	*	*	*	ns	*	*
Time	*	*	*	*	*	*	*	*	*	*
<b>Treatment*Time</b>	ns	*	ns	*	*	ns	*	ns	*	*

ns means not significant; \* means significant at  $p \le 0.05$ 

Overall, CBZ and DEET concentrations were greatest in the upper soil layer and gradually decreased with depth until no different were observed between the lower soil depths. A different trend was observed for CAF: it was not detected at depths of 0.10 m or 0.30 m in all treatments in either year. As for DCF, it was only detected at a depth of 0.10 m in the second year, only for the BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, and BC<sub>0</sub>CP<sub>7.5</sub> treatments, and only on the last two sampling days (Days 91 and 111). A similar pattern of greater levels being present in the topsoil layer was found for TCS measurements.

Thus, overall, at a depth of 0.10 m three different accumulation patterns were seen in the wastewater-irrigated soil: (*i*) high mobility (*e.g.*, CBZ and DEET), transport in the second year (*e.g.*, DCF), and slow to no movement, never detected at a depth of 0.10 m (*e.g.*, CAF).



**Figure 5.3:** PPCP concentrations (ng g<sup>-1</sup>) in surface soil in both years. The different superscripted lowercase letters in each column represent a significant difference at  $p \le 0.05$ . values are mean  $\pm$  standard error of three replicates. (A) CAF-2017, (B) CAF-2018, (C) CBZ-2017, (D) CBZ-2018, (E) DCF-2017, (F) DCF-2018, (G) DEET-2017, (H) DEET-2018, (K) TCS-2017, and (L) TCS-2018.

	Day 41	Day 71	Day 91	Day 111	Day 41	Day 71	Day 91	Day 111
CBZ	Year 1	2	5	5	Year 2	5	5	5
$BC_0CP_0$	1.12±0.81ab	12.61±1.90a	24.23±4.27a	14.13±4.25a	52.43±18.58a	56.81±13.53a	55.02±2.54a	70.27±20.18a
$BC_1CP_0$	0.37±0.091b	8.29±3.67a	18.72±5.49a	15.82±7.87a	49.43±29.13ab	25.36±12.81ab	30.58±14.57ab	49.22±6.45ab
BC <sub>3</sub> CP <sub>0</sub>	0.89±1.05ab	2.09±1.51b	1.00±0.63b	1.82±0.34bc	6.65±4.28b	12.18±10.88b	13.16±11.91b	36.18±15.83ab
BC <sub>0</sub> CP <sub>7.5</sub>	2.40±0.52a	1.49±1.08b	$5.48 \pm 0.48 b$	11.86±3.33ab	19.36±4.90ab	49.74±2.01a	21.69±13.96ab	49.30±24.14ab
BC1CP7.5	0.33±0.28b	0.42±0.10b	1.30±0.80b	1.29±1.06bc	24.90±20.29ab	49.29±23.24a	22.93±19.57ab	10.00±2.33b
BC <sub>3</sub> CP <sub>7.5</sub>	0.13±0.00b	0.48±0.52b	0.81±0.65b	0.64±0.42c	14.77±3.42ab	36.37±1.83ab	7.95±1.42b	25.50±7.40b
DEET	Year 1				Year 2			
$BC_0CP_0$	10.69±1.27a	10.85±2.17a	7.44±1.31b	4.83±0.73a	6.05±1.31b	8.26±0.96a	8.91±2.54a	23.97±4.75a
$BC_1CP_0$	8.55±0.87a	9.02±0.45a	14.71±0.88a	7.91±0.93a	19.84±7.76a	4.66±0.64ab	17.05±2.31a	11.64±2.39bc
$BC_3CP_0$	7.29±3.05a	10.79±5.86a	3.14±1.50bc	3.27±1.17a	7.27±4.19b	7.01±5.24ab	11.93±9.38a	5.80±2.97c
BC <sub>0</sub> CP <sub>7.5</sub>	10.66±2.76a	4.15±2.02a	3.93±1.89bc	4.38±3.51a	3.32±1.32b	8.32±5.23ab	7.62±4.24a	8.06±2.61bc
BC1CP7.5	7.79±1.20a	6.90±3.03a	3.59±3.17bc	4.24±2.91a	10.08±4.41ab	11.92±5.99ab	10.87±3.83a	12.46±2.38bc
BC <sub>3</sub> CP <sub>7.5</sub>	7.33±0.46a	6.55±1.32a	1.89±0.38c	2.98±0.44a	6.73±3.81b	1.81±0.55b	13.22±9.40a	14.30±2.05b
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**Table 5.5:** CBZ and DEET concentration (ng g<sup>-1</sup>) in 10 cm soil depth.

The different superscript lowercase letters in each column represent a significant difference at  $p \le 0.05$ .

values are mean  $\pm$  standard division of three replicates.

The soil concentration of PPCPs significantly increased with additional irrigation events, as confirmed by significant time effect ( $p \le 0.05$ ; **Table 5.4**) for all PPCPs in both years. Treatment also had a significant effect on the overall statistical model for CBZ, TCS and DEET in both years, and CAF in the year-2, but was not significant for DCF in either year. More specifically, for:

- CAF: In both years, the concentration of CAF ([CAF]) at the soil surface remained unaffected by a treatment × time interaction; however, the time effect was significant in both years, as were treatments effects in Year 2 (Table 5.4). In Year 1 at Days 71 and 91 (Figure 5.3), the [CAF] at the soil surface was greater under the BC<sub>3</sub>CP<sub>7.5</sub> treatment (*p* ≤ 0.05) than any other treatment except BC<sub>1</sub>CP<sub>7.5</sub>, while in Year 2, the [CAF] under BC<sub>0</sub>CP<sub>7.5</sub> was lower (*p* ≤ 0.05) than that under BC<sub>3</sub>CP<sub>0</sub> on Day 41 and lower (*p* ≤ 0.05) than that under BC<sub>0</sub>CP<sub>7.5</sub> on Day 91.
  - CBZ: In both years, time and treatment effects, along with the treatment × time interaction, had significant effects on the CBZ concentration ([CBZ]) at the surface soil (Table 5.4).
     Moreover, a treatment × depth interaction occurred for [CBZ] in both years. The Year 1 soil

surface [CBZ] was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>7.5</sub> than BC<sub>0</sub>CP<sub>0</sub> on Days 71 and 111, and was higher ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>0</sub> than BC<sub>0</sub>CP<sub>0</sub> on Day 111(**Figure 5.3**). A similar trend was observed in Year 2, when [CBZ] at the surface soil was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub> on Days 41, 91 and 111. A depth of 0.10 m, [CBZ] showed a distinctly different trend than at the surface (**Table 5.5**). In Year 1, the [CBZ] was lower ( $p \le 0.05$ ) under BC<sub>3</sub>CP0, BC<sub>1</sub>CP<sub>7.5</sub> and BC<sub>3</sub>CP<sub>7.5</sub> than BC<sub>0</sub>CP<sub>0</sub> or BC<sub>1</sub>CP<sub>0</sub> on Days 71, 91, and 111, while in Year 2, the [CBZ] under BC<sub>3</sub>CP<sub>7.5</sub> was lower ( $p \le 0.05$ ) than that under BC<sub>0</sub>CP<sub>0</sub> on Days 91 and 111, and [CBZ] under BC<sub>3</sub>CP<sub>0</sub> was lower ( $p \le 0.05$ ) than that under BC<sub>0</sub>CP<sub>0</sub> on days 41, 71 and 91. However, at a depth of 0.30 m, treatments had no significant effect on [CBZ] in either year.

- DCF: In both years, the concentration of diclofenac ([DCF]) at the soil's surface showed a significant effect of time, but not treatment or the treatments × time interaction (Table 5.4). At a depth of 0.10, DCF was only detected for the BC<sub>0</sub>CP<sub>0</sub>, BC<sub>1</sub>CP<sub>0</sub>, and BC<sub>0</sub>CP<sub>7.5</sub> treatments, and that only on the last two sampling days (day 91 and 111) of Year 2. At a depth of 0.30 m, no DCF was detected in either year. In surface soil, the only significant difference in [DCF] in Year 1 occurred on Day 71, when [DCF] under the BC<sub>0</sub>CP<sub>7.5</sub> w treatment was greater (*p* ≤ 0.05) than under BC<sub>0</sub>CP<sub>0</sub>. Similar trends in [DCF] were observed in Year 2, but no significant differences were detected (Figure 5.3). However, there were time effects, *i.e.*, between soil sampling dates.
- DEET: In both years, the effects of time, treatment and the treatment × time interaction on DEET concentration ([DEET]) at the soil surface were significant (Table 5.4). Moreover, in both years, a significant treatment × depth interaction occurred for [DEET]. At the soil surface the Year 1 [DEET] was greater (p ≤ 0.05) under BC<sub>3</sub>CP<sub>0</sub> than under BC<sub>0</sub>CP<sub>0</sub> for all sampling

days, and was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub> on sampling days 41, 71 and 111 (**Figure 5.3**). In Year 2, a similar trend was observed for [DEET] at the soil surface: [DEET] was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>7.5</sub> than BC<sub>0</sub>CP<sub>0</sub> on all sampling days, and was greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>0</sub> than BC<sub>0</sub>CP<sub>0</sub> on sampling Days 41, 71 and 91. The [DEET] at a depth of 0.10 m depth showed a different trend than at the soil surface (**Table 5.5**). In year 1, a lesser ( $p \le 0.05$ ) [DEET] was measured under BC<sub>3</sub>CP<sub>7.5</sub> than BC<sub>0</sub>CP<sub>0</sub> or BC<sub>1</sub>CP<sub>0</sub> in Day 91. Comparatively, in Year 2, a lesser ( $p \le 0.05$ ) [DEET] was measured under BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub> on Days 71 and 111, and a lesser ( $p \le 0.05$ ) [DEET] was found under BC<sub>3</sub>CP<sub>0</sub> than BC<sub>0</sub>CP<sub>0</sub> on Day 111. At a 0.30 m depth, treatments had no effect on [DEET] in either year.

TCS: While in both years TCS was never detected at a 0.10 m depth, the concentration of Triclosan ([TCS]) at the soil surface was significantly influenced by time and treatment factors, as well as their interaction (Table 5.4). In Year 1, on sampling Days 41 and 91, [TCS] under BC<sub>1</sub>CP<sub>7.5</sub> was greater (*p* ≤ 0.05) than under BC<sub>0</sub>CP<sub>0</sub>. In Year 2, on sampling Days 91 and 111, the [TCS] under BC<sub>1</sub>CP<sub>7.5</sub> or BC<sub>1</sub>CP<sub>7.5</sub> were greater (*p* ≤ 0.05) than under BC<sub>0</sub>CP<sub>0</sub> or BC<sub>1</sub>CP<sub>0</sub>.

#### 5.5 Discussion

Earlier studies have shown that in the process of making biochar, pyrolysis temperatures exceeding 400°C led to a greater aromaticity and hydrophobicity of biochar, a greater specific surface area (SSA), and a substantial amount of internal porosity (Uchimiya et al., 2011). The porous structure, relatively high specific surface area, and abundant surface functional groups make biochar an effective and low-cost adsorbent for contaminants (Wang et al., 2019). Scanning electron microscopy (SEM) allows the study of the morphology of solid particles. **Figure 5.3** [(a)-(f)] shows SEM micrographs of the surface of biochar and compost particles. The morphological

surface texture of compost was clear flatter than that of the biochar, SEM images showing that at all scales of magnification the number of nano-pores in the biochar surface largely exceeded that of the compost material. Nano-pores are reported to afford more sorption sites and exhibit high sorption energies, which has a significant impact on a material's sorption behavior with respect to organic contaminants (Pignatello and Xing 1996). The biochar's heterogeneous surface and greater porosity could be directly linked to its greater processing temperature compared to compost. The observed pores in the biochar images represent large macropores which can allow adsorbates to pass into the biochar's microporous system (Correa-Navarro et al., 2019).

With respect to the FTIR spectra of the biochar and compost (**Fig. 5.2** and **Table 5.3**), significant bands at 3337.13 cm<sup>-1</sup> confirmed the presence of oxygen-containing groups in both amendments. This is likely why the sorption of CAF, CBZ and DEET increased under biochar amendment of the soil and why it suffered a lesser impact that with a compost amendment (Chu et al., 2019; Naghdi et al., 2019). This lesser impact under biochar amendment likely resulted from different chemical structures of the functional groups of the different amendments, leading to a significant interaction of hydrophobic compounds with compounds bearing functional aromatic ring groups, such as the C=C.

Biochar works better than compost due to the structure of the surface functional groups of CBZ, DEET and CAF molecules. The CBZ molecule has three hydrophobic aromatic rings and two hydrophilic functional groups, an O=C and an amino group (NH<sub>2</sub>), which can react to form hydrogen bonds with the biochar. The FTIR peak at 1599.37cm<sup>-1</sup> was assigned to aromatic rings (Jindo et al., 2014) while the peak recorded at 3337.13 cm<sup>-1</sup> as determined in previous studies (Naghdi et al., 2019; Chu et al., 2019) was assigned to alcohol, O-H stretching and phenolic groups' C-O stretching. The DEET molecule has three CH<sub>3</sub> in addition to one aromatic ring, which

are considered hydrophobic sides, and a single O=C hydrophilic side (one H-bond donor) (**Table 5.1**)

The effects of barley straw biochar and compost soil amendments on soil properties were inconsistent (Table 5.2). Compared to adding biochar, compost amendment of the soil significantly increased the soil's DOC and pH at both depths, as documented previously in Table 4.4. In contrast, the total organic carbon (TOC) increased along with the rate of biochar amendment rate, being significantly greater ( $p \le 0.05$ ) under BC<sub>3</sub>CP<sub>0</sub> and BC<sub>3</sub>CP<sub>7.5</sub> than under BC<sub>0</sub>CP<sub>0</sub>. These results concurred with those of other studies (Beesley et al., 2014; Egene et al., 2018) that reported increases in DOC as a result of compost application. Likewise, Rodríguez-Vila et al. (2016) found that soil amendment with compost increased the soil's DOC to a greater extent than did biochar and attributed this increase to greater humification under a compost amendment. A similar trend was observed by Pump et al. (2019); however, the effect of compost on pH varies with the organic material used for composting (Tibu et al., 2019). Our study showed that compost derived from green and table waste is effective in increasing pH. In terms of TOC, the works of Hu et al. (2020) and Jiang et al. (2021) showed a significant increase in TOC at greater straw biochar amendment rates, which the latter authors attributed to the biochar amendment increasing the TOC mainly through an increase in the non-labile soil carbon content.

The process of chemical partitioning of organic chemicals, such as PPCPs, between the water and solid phase (*i.e.*, soil), is termed sorption (Schwarzenbach et al., 2003). The sorption behavior of pharmaceuticals is important in terms of their environmental impacts as it affects the transfer and distribution of compounds between phases, ultimately determining their mobility, bioavailability, and availability of the compound for degradation (Thiele-Bruhn et al., 2003). It is the bioavailable fractions that have the potential to be taken up into terrestrial organisms. In

general, the physicochemical properties of the PPCPs, such as their octanol-water partition coefficient ( $K_{ow}$ ), are important parameters in determining their adsorption to soil (Diaz-Cruz et al., 2003).

Overall, the extent to which PPCPs were transported downward into the soil by wastewater irrigation was minor. This was likely due to the chemicals' adsorption being affected by the soil amendments associated with the soil particles, along with degradation by soil microorganisms. Assessing the impact of biochar on the behaviors of PPCPs in soils allows an evaluation of their potential bioavailability for plant uptake and biodegradation. Increasing biochar application rates decreased the levels of DEET, CBZ and CAF below the soil surface. Caffeine and triclosan were both retained in the topsoil. Diclofenac was retained in the topsoil during Year 1 but began being transported downwards in Year 2, indicating that at low concentrations it was adsorbed by the soil, but at higher concentrations it became mobile. Carbamazepine and DEET were transported downwards in the soil to a depth of 0.30 m in both years. The sorption capacities of PPCPs are therefore the main determinant of their fate and transport within the soil-plant system. Sorption of PPCPs by soil generally reduces their uptake; however, irrigation or rain can cause adsorbed chemicals to be released into the soil to maintain soil equilibrium, allowing for plant uptake, or leaching (Carter et al., 2014; Li et al., 2019).

The high sorption capacity of biochar may prevent the release of organic contaminants with higher sorption capacities (*e.g.*, CAF, CBZ and DEET), explaining the treatment effect of biochar amendment on these contaminants. Alternatively, PPCPs with low sorption capacity often remain in solution and have a greater susceptibility for plant uptake and transport through leaching. Furthermore, the sorption capacities of PPCPs are dependent on the soil type, with dissociation constants (k<sub>d</sub> soil) of PPCPs varying with soil types (Franco et al., 2008; Barron et al., 2009).

Therefore, the fate and transport of PCPPs in the soil system is collectively determined by the psychochemical properties of both the PPCPs and soil. The fate and transport of PPCPs in the soil plant system is also influenced by the degradation of PPCPs through abiotic (*e.g.*, hydrolysis and photolysis) and biotic (*e.g.*, microbial) degradation (Fu et al., 2019). Accordingly, the K<sub>d</sub> for each PPCP varies according to the soil, the PPCP's physiochemical properties, as well as the soil's microbial community, pH and moisture (Dodgen et al., 2014; Monteiro et al., 2009). Enzymes exuded in the plant rhizosphere may also have an impact on sorption dynamics by increasing biodegradation through enhanced microbial activity (Monteiro et al., 2009; Lefevre et al., 2013). Introduction anti-microbial agents into the soil system through wastewater irrigation could alter microbial populations and associated biodegradation of PPCPs (Fu et al., 2016).

The special surface properties and physical structure of biochar make it a promising sorbent for organic compound. It acts through various mechanisms, including hydrophobic interaction,  $\pi$ - $\pi$  electron-donor-acceptor interaction, electrostatic attraction, pore filling, partitioning into the uncarbonized fraction, and formation of charge-assisted hydrogen bonding with surface oxygen groups (Ahmed et al., 2017; Qin et al., 2020). The retardation of pollutants is a function of the distribution coefficient, along with the soil's bulk density and porosity. One can expect a significant subsurface retardation of non-polar compounds, *i.e.*, those with high a log K<sub>ow</sub> value, and accordingly, a high log K<sub>oc</sub> (organic carbon sorption coefficient) (**Table 5.1**).

In general, CBZ has been found to be largely adsorbed in the topsoil (0-0.05 m), and less in the second soil layer, but not at all in deeper (>0.25 m) soil layers (Arye et al., 2011). However, sorption has been shown to be reversible and accumulation of CBZ in topsoil layers is greater in soils enriched in organic matter (Paz et al., 2016). Williams et al. (2015) found that biochar amendment decreased PPCPs concentration in pore water and also decreased their bioavailability and uptake. Studies have shown that due to high surface area, micropore volume and numerous polar functional groups, biochar can adsorb hormones (Zhang et al., 2013b). This may occur since higher pyrolysis temperatures lead to increased surface area and micro porosity, allowing for more effective sorption. Even small amounts (0.1%) of biochar in soil have been able to reduce the bioavailability of certain organic contaminants (Zhang et al., 2013b).

Biochar has a porous structure, similar to activated carbon, which is often employed as an efficient sorbent for contaminants (Chia et al., 2012). The physiochemical properties of biochar may influence its adsorption kinetics. Uchimiya et al. (2011) found that O-containing carboxyl, phenolic and hydroxyl surface function groups may bind emerging contaminants. However, the sorption of emerging contaminants in soil is complicated by numerous physiochemical factors and can be highly variable depending on the presence of competitors (organic matter, metals and ions), as well as the amount and types of sorbents and adsorbate (Wang et al., 2013b).

Compost amendment and WW irrigation are an important source of dissolved organic carbon in soil. Dodgen and Zheng (2016) found that the level of DOC in lagoon irrigation water was highly correlated with the increase in half-life of CAF (among other PPCPs) in the soil, so irrigation water DOC may contribute to CAF's persistence in the irrigated soil. Compost amendment treatments had no significant effect on DCF or TCS levels in the soil; however, the mobility of CAF, CBZ and DEET were affected by increasing rates of biochar amendment. Compost had no impact on the soil mobility of any of the PPCPs studied.

Based on our findings, more research is needed to meet the organic compound targets in wastewater-irrigated soil. Xiang et al. (2020) concluded in their review that modifications made to biochar that increase its (SSA), reaction activity, or its ability to form functional groups are important. Once modified, engineered biochar can serve as an adsorbent to remove specific contaminants. Its ability to do so is controlled by various ion exchange mechanisms, adsorption, surface precipitation, surface complexation etc. From our results the biochar's functional groups played a significant role in retaining some of the target compounds that bound to the biochar surface. As a result, it is important to choose the right biochar modification methods for adsorption of organic contaminants based on their physicochemical properties. Metal oxide, acid-base modification, and metal salt modification are now the most prevalent ways for improving biochar's adsorption capability to organic contaminants (Cheng et al., 2021).

#### 5.6 Conclusions

PPCPs with low sorption capacities are of high concern in agricultural systems as they are more prone to be taken up by plants or to leach into groundwater or re-emerge in the greater environment. In conclusion, our study found that biochar can reduce the mobility of some PCPPs (CAF, CBZ and DEET) in sandy soils. The effectiveness of biochar in retaining PCPPs in the topsoil increased, with the 3% biochar amendment rate retaining more CAF, CBZ, and DEET. In the case of diclofenac, this study showed that once it reached higher concentrations by year 2, it became more mobile. CAF and TCS were retained in the topsoil under all treatments. Further research should aim to broaden our understanding of PCPP fate and transport in soil cropping systems by looking at plant uptake as well as their mobility risks. It appears that an application rate of 3% biochar to a cropping system might be beneficial in reducing PPCP mobility and subsequent groundwater and environmental contamination. More work is also needed to understand how the soil mobility of PPCPs correlates to their uptake by plants.

# 5.7 Acknowledgements

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#### **Connecting Statement to Chapter 6**

In the literature review (Chapter 2), I reported the effects of nanoparticles in the environment as detected in wastewater, especially the widely used TiO<sub>2</sub>-NPs, showing their potential to interact with heavy metals.

The previous manuscript (Chapter 3) investigated the effects of soil amendments (*e.g.*, biochar alone or in combination with compost) on the plant uptake of heavy metals and soil mobility. while Chapter 6, evaluates the presence of TiO<sub>2</sub>-NPs to minimize plant uptake of heavy metals and minimize their soil mobility.

The following manuscript (Chapter 6) is under preparation and is to be submitted to the Journal of NanoImpact. The manuscript is co-authored by Prof. Kevin J. Wilkinson a professor in the Department of Chemistry, University de Montreal; Prof. Shiv Prasher, research supervisor, and Prof. Stéphane Bayen, research Co-supervisor, Ms. Emma C. Anderson, an MSc scholar in the Department of Bioresource Engineering, Dr. Eman ElSayed in the Department of Bioresource Engineering, and Dr. Saji George in the Department of Food Science, McGill University. The original draft has been modified to ensure consistency with the thesis format, and the cited references are listed in the reference section (Chapter 10).

# 6 Chapter 6: Impact of wastewater borne TiO<sub>2</sub>-NPs on metal uptake by potato plants receiving synthetic wastewater irrigation

#### 6.1 Abstract

Increasingly considered as a source of water for irrigation, wastewater (WW) can pose risks due to potential uptake of contaminants in it by crops. WW can be a source of metals and organic contaminants that are known to have harmful implications for human and environmental health. The detection of nanoparticles (NPs) in WW has raised questions about their potential interactions with other co-contaminants and their effects in soil-water systems (e.g., WW irrigated agriculture). Titanium dioxide nanoparticles (TiO<sub>2</sub>-NPs), a type of NPs commonly used in industrial and consumer products and reported to be present in WW, could potentially influence the mobility of contaminants in soils and the uptake of metals by crops. Accordingly, a field lysimeter study was conducted for two years (2017 and 2018) in order to investigate the impacts of TiO<sub>2</sub>-NPs on the mobility of metals (Cd, Cr, Cu, Fe, Pb and Zn) and their uptake by potato plants (Solanum tuberosum L. cv. 'Russet Burbank'). Potatoes were grown in a sandy soil under controlled conditions and irrigated with synthetic WW or WW+TiO<sub>2</sub>-NPs. At harvest, potato tubers and plant parts were analyzed for their metal concentrations by inductively coupled plasma mass spectrometry (ICP-MS), while inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to measure metals in the soil samples. The presence of 1 mg TiO<sub>2</sub>-NPs  $L^{-1}$  in the WW irrigation water significantly ( $P \le 0.05$ ) reduced the uptake of Cd, Cu, and Zn into potato flesh, skin, and roots in both treatment years, but had no significant effect on Cr, Pb and Fe uptake into any plant parts. The presence of TiO<sub>2</sub>-NPs in WW appeared to reduce the bioavailability of Cd, Cu and Zn in the soil.

Keywords: Food Crops, Metals, Plant Uptake, TiO<sub>2</sub>-NPs, Wastewater Irrigation.

# 6.2 Introduction

Water scarcity is increasing globally with over 2 billion people lacking access to clean water (Alois, 2007). This critical situation is compounded by: (*i*) growing global populations, heightened global food demand, and demands on freshwater for irrigation (DESA, 2014); and (*ii*) the adverse effects of urbanization and industrialization on water quality and human health. The agricultural sector is one of the primary users of freshwater (Ardakanian et al., 2016). Although only 20% of arable land is irrigated, irrigated land accounts for 40% of global food production (Ardakanian et al., 2016). Globally, 80% of the wastewater flows back into ecosystems, without being treated or reused (Connor et al., 2017; Corcoran, 2010), which can threaten the health of vital ecosystem services and human populations living downstream. However, 70% of the wastewater is treated in developed countries while only 8% is treated in under-developed countries (Connor et al., 2017). These figures amplify the issues of water scarcity and security within populations, especially in the developing world.

Wastewater reuse is a preeminent approach to combat water scarcity problems where pollutants concentrations are decreased in wastewaters, prior to their release into the environment, (Ghernaout and Ibn-Elkhattab, 2020). Wastewater reuse is also an integral part of the circular economy, where wastewater is seen and used as a resource, due to the water and nutrients it contains (Fito and Van Hulle, 2020). Reuse of wastewater through crop irrigation has the potential to increase agricultural food production, promote freshwater conservation, and limit the harmful practice of openly discharging untreated wastewater into the environment (Qadir et al., 2010). Wastewater irrigation can also help combat the global decline in soil fertility by increasing soil organic carbon content; increasing the availability of nitrogen, phosphorus, and potassium; increasing crop production, and improving the physical, chemical and biological properties of soils
(Baldantoni et al., 2010; Jalali and Arfania, 2010; Marofi et al., 2015; Siebe, 1998; Tabari and Salehi, 2009). Therefore, irrigation with wastewater can address increasing water scarcity and falling soil fertility problems (Connor et al., 2017; Maryam and Büyükgüngör, 2019).

In contrast to its potential benefits, wastewater irrigation also poses major risks. Without adequate treatment *ex-situ* or *in-situ*, wastewater irrigation can introduce a combination of inorganic and organic contaminants into the environment and ultimately into human food, ranging from endocrine disruptors to carcinogenic, mutagenic and teratogenic compounds (Shakir et al., 2017; Xing et al., 2007). These contaminants can be toxic for both humans and wildlife (Lopes et al., 2015). Beyond human and wildlife health concerns, certain contaminants hinder crop growth and yields when applied above certain levels (Ji et al., 2017), potentially impacting farmers' incomes and livelihoods. Choosing a treatment technology to remove metals, however, depends on a number of factors, including their concentrations, wastewater components, operating costs, operating mode and environmental impact (Fu and Wang, 2011). With their large surface area, simple processing, unsaturated functional groups and reactivity, NPs are a new type of material that have recently been found in wastewater and may act as immobilizers and sorbents.

NPs are particulate materials with a diameter inferior to 100 nm (Cai et al., 2017). Their small size confers to them a high surface to volume ratio and enhancing surface interactions with biological systems, often with detrimental outcomes in human and other environmental organisms (Thomas et al., 2011; Nel et al., 2006). NPs have a wide range of effects in agriculture (Asli and Neumann, 2009), including: soil modification, nutrient supply, and disease suppression. The accumulation of NPs and their biotransformation in soils and sediments occurs more so in soil systems (Tou et al., 2017). NP-induced phytotoxicity in both liquid and solid substrates has been

widely documented in both laboratory and greenhouse conditions over the last decade (Rizwan et al., 2017).

One of the most used metallic NPs, TiO<sub>2</sub>-NPs, are found in sunscreens, cosmetics, paints as well as organic pollutant immobilizers (Cai et al., 2017). Certain plant species can take up, accumulate and translocate TiO<sub>2</sub>-NPs (Cai et al., 2017), while not suffering phytotoxic effects (Song et al., 2013). Other studies have noted improved growth in the presence of TiO<sub>2</sub>-NPs. For example, spinach (*Spinacia oleracea* L.) growth was found to be accelerated by the effect of TiO<sub>2</sub>-NPs on light absorption and promotion of rubisco enzyme activity (Nair et al., 2010). Further studies have suggested that there may be a threshold up to which TiO<sub>2</sub>-NPs can stimulate growth and above which they may inhibit growth (Song et al., 2013). Indeed, at high concentrations, TiO<sub>2</sub>-NPs were found to significantly reduce Pb uptake by rice (Cai et al., 2017). In soils, NPs can immobilize metals through various mechanisms such as reduction, physical sorption, chemisorption and co-precipitation (Mahdavi et al., 2015a; Mahdavi et al., 2013).

However, NPs can adversely impact plant growth in crops; indeed, several investigations on the ecotoxicological effects of relatively high concentrations of NPs have been undertaken to determine their potentially hazardous effects (Holden et al., 2016). The literature on the impact of TiO<sub>2</sub>-NPs on plant yield is mixed, with some finding TiO<sub>2</sub>-NPs stimulates plant growth (Hong et al., 2005; Nair et al., 2010; Yang et al., 2006) and others finding it inhibits plant growth (Song et al., 2013). However, it is suggested that TiO<sub>2</sub>-NPs only inhibit plant growth at concentrations over 5 mg/L in water solution (Song et al., 2013), which is higher than what would likely be found in most wastewaters. Alternatively, others have found that NPs can enhance crop production in polluted soils through nanoremediation/phyto-nanoremediation (El-Ramady et al., 2017; Wang et al., 2016a). In particular, El-Ramady et al. (2017) cited the ability of TiO<sub>2</sub>, zero-valent iron, carbon nanotubes and ZnO to minimize the uptake of metallic pollutants by plants, reducing their toxicity both to the plants and their human consumers. NPs can immobilize metal(loids) (*i.e.*, Cd, Pb, As and Cr) in soils, reducing metal mobile metal fractions (Mallampati et al., 2013). They can also impact the metal redox potential, potentially converting metals into less toxic species (Abhilash et al., 2016).

Given the increasing presence of TiO<sub>2</sub>-NPs in WW and the environment, this study investigated how TiO<sub>2</sub>-NPs influence the uptake of metals by crops and their mobility in the soil. Specifically, the study aimed to shed light on how the interactions between TiO<sub>2</sub>-NPs and metals commonly found in wastewater effluents (Cr, Cd, Pb, Fe, Zn, Cu; Mehdipour et al., 2015) could affect potatoes. Potatoes were chosen as they represent a staple global food crop, subject to a moderate risk of metal accumulation in contaminated soils (Zhou et al., 2016). This is the first study that examines the effect of TiO<sub>2</sub>-NPs, present in heavy-metal containing wastewater, on the mobility and uptake of multiple heavy metals in a soil-plant system.

# 6.3 Materials and Methods

## 6.3.1 Experimental Setup

The field study was conducted in lysimeters located at the Macdonald Campus of McGill University in Sainte-Anne-de-Bellevue, QC, Canada (lat.  $45^{\circ}24'48.6"$  N and long.  $73^{\circ}56'28.1"$  W). The PVC lysimeters (1 m height  $\times$  0.45 m inner diameter) were sealed at their bottoms with a PVC sheet and each provided with a perforated drainage pipe to collect the leachate. Lysimeters were filled with a sandy soil (**Table 4.1**), obtained from the Macdonald Campus Farm of McGill University. Three treatments (freshwater, wastewater control, and wastewater + TiO<sub>2</sub>-NPs) were triplicated and randomly assigned to an array of nine lysimeters. Freshwater was used to see if NPs

can reduce the metal concentrations to the level of freshwater, in comparison to the wastewater control.

Potato seed-tubers (cv. 'Russet Burbank'), stored at 8-10°C, were germinated by placing them in a cardboard box at room temperature, two weeks before planting. On the day of planting, one tuber was planted 0.10 m deep in the center of each lysimeter. Background soil samples were collected prior to planting/ or irrigating (Day 0). The lysimeters were kept in a white canvas tent to prevent precipitation from entering the lysimeters. An array of ten 60-W LED bulbs were installed above the lysimeter array, in order to supplement natural light. The quantum flux in the tent was quantified using a MQ-200 Quantum Flux meter (Apogee Instruments Inc., Logan, Utah). Weather data (daily average relative humidity, daily high and low temperatures, precipitation, and wind speed) were collected from the Sainte-Anne-de-Bellevue weather station located at lat. 45°25'38.000"N, long. 73°55'45.000"W. Metal (Cd, Cr, Cu, Fe, Pb, and Zn) concentrations in the soil were measured prior to the onset of the experiment (2017). Cr, Cu, Fe and Zn were detected in the soil but Cd and Pb levels were below the limit of detection of the ICP-OES (**Table 4.1**).

At the end of the growing seasons, core sample sections were taken from each lysimeter for depths of 0-20 mm, 20-40 mm, 40-60 mm, 60-80 mm and 80-100 mm. The potatoes were harvested 120 days after planting, once tuberization was complete. Aboveground biomass (AGB) was chopped off at the soil surface with a knife and weighed. The length of the longest shoot was recorded. The AGB was separated into stems and leaves. Tubers were harvested, weighed and counted. All plant parts were stored in paper bags and brought to the laboratory for analysis. Potato tissues were thoroughly washed with deionized water, drained and blotted dry. Tubers were peeled. Tuber flesh was dissected longitudinally and further diced into roughly 10 mm  $\times$  10 mm cubes. Potato tissues were oven-dried ( $60^{\circ}$ C) for two days within the brown paper bags. Dried samples were ground in a stainless-steel coffee grinder and with a ceramic mortar and pestle.

The soil was left in the lysimeters after the first year's harvest for use in the second year of the experiment. During the winter, lysimeters were covered with plastic bags to prevent material from entering or leaving.

## 6.3.2 Preparation of TiO<sub>2</sub>-NPs and Synthetic Wastewater for Irrigation

TiO<sub>2</sub>-NPs (21 nm particle size, 99.5% purity CAS No. 13463-67-7) were purchased from Sigma Aldrich (St. Louis, MO, USA) and very-low viscosity sodium alginate was obtained from VWR (Ville Mont-Royal, QC, Canada). Prior to being added to the wastewater, TiO<sub>2</sub>-NPs were dispersed in a 1000 mg L<sup>-1</sup> stock solution by first adding 100 mg of sodium alginate to 90 mL of deionized water, heating the solution to 80°C, adding 100 mg of TiO<sub>2</sub>-NPs, and topping up the volume to 100 mL with deionized water. The stock solution was then vortexed for 30s and sonicated for 10 min. The solution was sonicated again for 15-20 min, immediately prior to use. Forty mL of the stock solution was added to 40 L of irrigation water as the TiO<sub>2</sub>-NPs treatment, giving a final concentration of 1 mg L<sup>-1</sup> of TiO<sub>2</sub>-NPs, which is similar to a concentration previously detected in wastewater (Westerhoff et al., 2011).

A synthetic wastewater was prepared by dissolving metals and other compounds in a freshwater, in order to represent a worst-case scenario of wastewater based on reports in the literature (**Table 4.3**). All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Fisher Scientific (Waltham, MA, USA). Every ten days, each lysimeter was irrigated with 11.5 L of either freshwater or two treatments with synthetic wastewater - one synthetic wastewater alone and the other treatment mix with TiO<sub>2</sub>-NPs, every ten days, *i.e.*, eight times per season. The

irrigation volume was determined based on the water requirements (500-700 mm) and progress through the growing season (120 days) of the potato crop.

#### 6.3.3 Sample Extraction and Quantification

The soil pH was measured in the supernatant of a 1:2 mixture of soil to distilled water (Rayment and Higginson, 1992), following mixing on a shaker for 30 minutes. Measurements were performed using a pH electrode (Accumet pH meter model AB15, Fisher, Scientific, USA). Electrical Conductivity (EC) readings were done using a Radiometer CDM 83 Instrument (Radiometer; Copenhagen, Denmark) (Hendershot et al., 1993b). Soil dissolved organic carbon was determined in soil samples using a TOC analyzer (Sievers InnovOx Laboratory, GE Power and Water USA). Cation exchange capacity was measured using the BaCl<sub>2</sub> method, as described by Hendershot et al. (1993a). The SOM was quantified by loss on ignition (Schulte et al., 1991).

To quantify metals in the soils and plant tissues, samples were first digested using hot nitric acid (EPA, 1996; Kargar et al., 2015). A homogenized 0.16 g sample was placed in a 15 mL polypropylene centrifuge tube to which 2 mL of concentrated nitric acid (trace metal grade, 70%) was added. The solution was then allowed to equilibrate overnight. Subsequently, samples were placed in a block digester (Fisher Scientific®, dry batch incubator) where the temperature was gradually increased to 80°C. Heating continued until the brown colour disappeared. The temperature was gradually increased to 120±5 °C and the solution allowed to digest for a further 5 hrs. Samples were then cooled for 15 minutes, transferred to 50 mL polypropylene centrifuge tubes and the solution diluted with deionized water to a volume of 50 mL. Digested soil samples were stored at 4°C prior to quantification by ICP-OES (Varian, Vista-MPX CCD simultaneous, Varian, CA, USA). Quantification of the metals in plant tissues was done by ICP-MS (Varian ICP820-MS or Analytik-Jena), given the expected low concentrations of metals in the different

potato tissues. Reference materials (SED98-04 and SED92-03, Environment Canada) and three blanks were added to all runs of the ICP-OES and ICP-MS to ensure quality control.

#### 6.3.4 Data Analysis

Soil properties and metals in the plant tissues were analyzed using one-way Analysis of Variance (ANOVA), considering treatment as the only factor. While the metal concentration in soil was assigned as a response variable and treatment and depth were assigned as fixed effects variables. Statistical analysis was performed using the general linear model (GLM) procedure of SAS 9.4 (SAS Institute Inc., Cary, NC) and test of significance was done using the Least Significant Difference test (LSD) where ( $p \le 0.05$ ).

#### 6.4 **Results**

#### 6.4.1 Effect of TiO<sub>2</sub>-NPs on the Physiochemical Properties of the Soils

Presence of  $TiO_2$ -NPs in the wastewater had no significant effect (p > 0.05) on the physiochemical properties (pH, CEC, DOC, SO, and EC) of the sandy soil, either at the soil surface or at 0.10 m depth. **Table 4.1** shows the properties of the soil, prior to the experiment, while **Table 6.1** shows the soil properties on the last day of the second growing season.

	pH	CEC	DOC	SOM	EC
		(cmol <sub>c</sub> kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(%)	(ds/m)
			Surface soil		
WW	5.01±0.1 <sup>a</sup>	1.79±0.29 <sup>a</sup>	13.17±0.86ª	2.8±0.64 <sup>a</sup>	222.33±39.67ª
NP	$5.08 \pm 0.07^{a}$	2.33±0.30 <sup>a</sup>	$13.78 \pm 2.87^{a}$	$2.6\pm0.55^{a}$	200.02±22.91ª
			0.10 m depth		
WW	5.26±0.15 <sup>a</sup>	2.62±1.24 <sup>a</sup>	12.62±0.75 <sup>a</sup>	2.72±0.19 <sup>a</sup>	170.66±36.55 <sup>a</sup>
NP	5.30±0.30 <sup>a</sup>	$3.44{\pm}1.81^{a}$	11.34±2.82 <sup>a</sup>	2.69±0.06ª	167.33±29.87 <sup>a</sup>

**Table 6.1**: Effect of treatments on soil properties after second season.

The values are the mean  $\pm$  standard error of 3 replicates: ( $p \le 0.05$ ).

#### 6.4.2 Effect of TiO<sub>2</sub>-NPs on the Mobility of the Metals in the Sandy Soil

The treatments and treatments\*depth interaction did not have a significant ( $p \le 0.05$ ) impact on metal concentrations, though metal concentrations did significantly ( $p \le 0.05$ ) vary with depth for Cd, Cu, Fe and Pb. Metal levels reported in **Table 6.2** for the second season were averaged across all layers. Although **Cd** was below ICP-OES detection limits in the background soil, due to its presence in the wastewater, it was measured in soil at the end of the treatment period. In the first year, Cd was found in the upper 0-80 mm layer but it was not detected in the 80-100 mm layer in either treatment (WW alone or WW+NP). In the second year of the experiment, Cd was detected in the 80-100 mm layer, indicating that Cd could have migrated downward with further application of the wastewater at the soil surface.

The concentration was nonetheless greatest in the topsoil (0-20 mm) layer, indicating that transport was slow. Indeed, the Cd concentration gradually decreased with depth in all treatments, in both years, though there was no significant difference between treatments at any depths.

		Maximum		0-20 mm	20-40 mm	40-60 mm	60-80 mm	80-100 mm
		Limit *						
		CCME	Eu					
Cd	WW	1.4	3	50.5±8.25	30.5±6.56	38.5±5.93	44.1±8.16	29.0±8.50
	NP			57.8±20.25	45.3±14.72	34.3±9.54	28.7±4.72	22.5±4.94
Cr	WW	64	150	30.6±2.78	33.0±9.01	29.5±3.41	27.1±2.37	23.4±2.39
	NP			37.9±8.00	29.6±2.46	29.7±3.78	31.2±4.69	26.9±7.30
Cu	WW	63	140	254.2±27.76	170.8±24.96	70.5±29.17	$62.2 \pm 24.40$	45.9±7.10
	NP			225.5±70.74	146.0±9.14	35.7±3.33	67.1±42.10	32.7±17.07
Fe	WW	n.a.	n.a	15766±2054	14398±1340	14795±1535	13468±385	12657±631
	NP			18241±2176	14147±656	14472±2088	14882±446	12750±1581
Pb	WW	70	300	366.9±75.91	131.8±113.43	144.4±150.17	73.8±38.46	37.9±29.67
	NP			383.6±164.48	139.6±68.72	99.7±102.80	$71.5 \pm 40.05$	44.6±25.25
Zn	WW	250	300	53.1±7.14	40.6±7.34	47.3±7.05	52.1±9.08	41.7±4.52
	NP			61.8±11.90	57.2±20.58	46.9±8.83	50.7±9.93	45.6±14.49

**Table 6.2**: Metal concentrations in soil samples collected at 5 layers after the last irrigation in year- 2.

Note \* maximum limit according to Canadian Council of Ministers of the Environment (CCME, 2007); EU: European Union (Meng et al., 2016). Concentrations are presented in mg kg<sup>-1</sup>. Where applicable, the values are presented as mean  $\pm$  standard deviation of 3 replicates. n.a., not available.

For **Cr**, a significant difference was observed in soil concentrations at the surface (0-20 mm) and at (80-100 mm), with higher concentrations at the surface. However, the concentrations of Cr between 20-80 mm were not significantly different from either 0-20 mm or 80-100 mm. For **Zn**, there were no significant (p > 0.05) differences between treatments, depths or treatment-depth interactions in either year. In contrast, for Cu, there was a significant ( $p \le 0.05$ ) difference in Cu concentration with depth, but the presence of TiO<sub>2</sub>-NPs had no significant effect. Cu concentrations were significantly greater in the 0-20 mm and 20-40 mm layers than other layers. Across all of the treatments in year 1, Cu was not detected in the 80-100 mm layer.

There was a significant ( $p \le 0.05$ ) difference in **Fe** concentration with depth, but no significant differences between treatments or the treatment-depth interaction at any depths. The Fe concentrations in the 0-20 mm layer were significantly different from those in the 20-40 mm, 60-80 mm, and 80-100 mm layers.

There was a significant ( $p \le 0.05$ ) difference in **Pb** concentration with depth, but no significant effect of the TiO<sub>2</sub>-NP treatment on Pb concentrations. The Pb concentrations were significantly greater ( $p \le 0.05$ ) in the 0-20 mm layer than in deeper layers.

Regardless of the treatments, the concentration of metals at the deeper depth of 80-100 mm was dependent upon the type of metal and the second year accumulation. For all treatments and in this soil layer, the Cd and Cu concentrations were below the LOD in year 1; however, Fe, Cr, and Zn were detected at fairly high concentrations.

## 6.4.3 Effect of TiO<sub>2</sub>-NPs on Metal Uptake

#### 6.4.3.1 Potato Tubers

Metal concentrations (mg kg<sup>-1</sup>) in potato tubers (flesh and skin) irrigated with freshwater and wastewater (with and without TiO<sub>2</sub>-NPs) are presented in **Table 6.3**. Again, the freshwater treatment was applied to see if NPs in wastewater could reduce metal concentrations in plant to the level of freshwater, in comparison to the wastewater control. Results for both years show that there was a significant effect of the presence TiO<sub>2</sub>-NPs on Cd and Cu concentrations in potato flesh and skin. In contrast, no significant differences were observed for Cr and Pb concentrations in the potato flesh, in either year, under the presence TiO<sub>2</sub>-NPs (p > 0.05). This suggests that that Pb was being held in topsoil and not being leached to the root depth. Although Cr appeared to be translocated into the plants, even for the background soils, its concentration in the potato flesh was not affected by wastewater irrigation.

No significant differences (p > 0.05) were observed in Fe or Zn concentrations in potato flesh among the presence TiO<sub>2</sub>-NPs and the control, suggesting that the pre-treated soil had naturally occurring Zn and Fe that was not significantly increased by wastewater irrigation in the first season. In the second year, the WW treatment showed significantly greater ( $p \le 0.05$ ) Fe concentrations in the tuber flesh than for the FW or NP treatments - the latter treatments were not significantly different from each other. Similarly, in the second year, the potato flesh showed significantly lower ( $p \le 0.05$ ) Zn concentrations for the FW, as compared to the WW and NP treatments, although these latter treatments showed no significant differences.

ts	at	Metals						
lant Par	Treatme							
Ч		Cd	Cr	Cu	Fe	Pb	Zn	
				Year 1				
Flesh	FW	$0.15 \pm 0.08^{b}$	$0.21\pm0.19^{a}$	6.79±2.11 <sup>b</sup>	16.33±4.98 <sup>a</sup>	0.16±0.22 <sup>a</sup>	13.88±3.30 <sup>a</sup>	
	WW	$1.50\pm0.96^{a}$	$0.11 \pm 0.00^{a}$	$11.61 \pm 1.73^{a}$	22.51±5.21ª	$0.24\pm0.17^{a}$	19.61±6.50 <sup>a</sup>	
	NP	$0.45 \pm 0.10^{ab}$	$0.08\pm0.04^{a}$	$7.41 \pm 0.69^{b}$	17.90±2.64 <sup>a</sup>	0.31±0.13 <sup>a</sup>	13.54±0.53 <sup>a</sup>	
Skin	FW	0.29±0.08°	$0.31\pm0.06^{a}$	$9.38 {\pm} 1.05^{ab}$	47.85±12.20 <sup>a</sup>	$0.12 \pm 0.04^{a}$	18.86±2.43 <sup>b</sup>	
	WW	11.29±0.81 <sup>a</sup>	$0.28\pm0.05^{a}$	$10.93 \pm 2.18^{a}$	77.46±21.06 <sup>a</sup>	0.41±0.22 <sup>a</sup>	39.39±12.72 <sup>a</sup>	
	NP	1.53±0.61 <sup>b</sup>	$0.24\pm0.07^{a}$	$7.63 \pm 0.84^{b}$	$69.45 \pm 26.66^{a}$	$0.22 \pm 0.02^{a}$	17.77±2.06 <sup>b</sup>	
				Year 2				
Flesh	FW	0.20±0.15°	$0.04\pm0.01^{a}$	$8.01 \pm 0.81^{b}$	16.81±0.18 <sup>b</sup>	<lod< th=""><th>15.10±1.95<sup>b</sup></th></lod<>	15.10±1.95 <sup>b</sup>	
	WW	5.30±1.37 <sup>a</sup>	$0.04\pm0.01^{a}$	$10.81 \pm 0.98^{a}$	26.25±1.37 <sup>a</sup>	<lod< th=""><th>26.10±3.51ª</th></lod<>	26.10±3.51ª	
	NP	3.04±0.81 <sup>b</sup>	$0.06\pm0.03^{a}$	9.33±0.53 <sup>ab</sup>	16.10±2.27 <sup>b</sup>	<lod< th=""><th>22.11±1.24<sup>a</sup></th></lod<>	22.11±1.24 <sup>a</sup>	
Skin	FW	0.34±0.09°	0.26±0.01 <sup>b</sup>	9.39±2.10 <sup>b</sup>	77.34±7.19 <sup>a</sup>	0.13±0.12 <sup>b</sup>	19.85±1.91 <sup>b</sup>	
	WW	59.37±19.64 <sup>a</sup>	$0.37 \pm 0.04^{a}$	$23.51 \pm 5.77^{a}$	134.72±87.14 <sup>a</sup>	2.32±0.01 <sup>ab</sup>	$101.46 \pm 27.90^{a}$	
	NP	21.29±13.00 <sup>b</sup>	$0.25 \pm 0.05^{b}$	17.28±3.36ª	$71.98{\pm}1.57^{a}$	$2.92{\pm}1.26^{a}$	$55.37 \pm 20.07^{b}$	

Table 6.3: Metal (Cd, Cr, Cu, Fe, Pb and Zn) concentrations in potato flesh and skin in both years.

The values are the mean  $\pm$  standard error of 3 replicates; for each potato tissue category, different letters signify a significant difference ( $p \le 0.05$ ) column wise within tissue, year and metal contaminant. Pb LOD was 0.037 (µg/g).

In both sampling years, Cd concentrations in potato flesh were significantly greater  $(p \le 0.05)$  in the WW treatments than for the FW treatment. Additionally, in year 2, Cd concentrations were significantly greater  $(p \le 0.05)$  following the WW treatment, as compared to the NP treatment, suggesting that the NPs in the wastewater were able to reduce Cd bioavailability, leading to reduced Cd concentrations in the tubers of potato plants irrigated with wastewater.

Cu levels in potato flesh were significantly greater ( $p \le 0.05$ ) in the WW treatment, as compared to the other treatments. Cu concentrations in the potato flesh were not significantly different for the FW and NP treatments, in either year. In year 2, the only significant difference was between the WW and FW treatments.

In both years, no significant differences were observed between Fe concentrations in potato skins for the different treatments. In year 1, no treatment effect was observed for Cr and Pb in the potato skins, whereas in year 2, the WW treatment showed a significantly greater (P $\leq 0.05$ ) Cr concentration than for either the NP or FW treatments, though the latter two treatments showed no significant difference. In contrast, in year 2, Pb skin concentrations under the NP and FW treatments were significantly different, but that under WW was not significantly different from either of the former treatments. In both years, the WW treatment showed greater ( $p \leq 0.05$ ) Cd concentrations in the skin than for either the FW or NP treatments. Overall, all treatments had Cd flesh concentrations that were significantly different from each other in both years. Accumulation of the Cd in the soil after two years of WW irrigation likely contributed to the high concentration of Cd in the skin in year 2.

In year 1, the Cu in the potato skin only showed a significantly difference between the WW and NP treatments, but, in year 2, no significant difference was observed between the NP and WW treatments, though they were both significantly different from the FW. In both years, the concentration of Zn in the skin following the WW treatment was significantly greater ( $p \le 0.05$ ) than in the FW or NP treatments, which showed no significant difference amongst themselves.

Notably, the presence TiO<sub>2</sub>-NPs significantly reduced ( $p \le 0.05$ ) the Cd and Zn concentrations in potato skin over both years in comparison to the WW treatment. Similar results were also obtained for the Cr skin concentrations in year 2 and Cu skin concentrations in year 1.

## 6.4.3.2 Potato Roots

In both years, the Cd and Zn root concentrations were greater ( $p \le 0.05$ ) under the WW treatment than under the FW and NP treatments, with all treatments having significantly different root concentrations (**Table 6.4**). For both years, the addition of NP to the WW reduced significantly (p< 0.05) Cd and Zn concentrations in the potato roots. Similar trends were observed for Cr, Fe and Pb concentrations in year 2- although there were no significant differences between the FW and NP; metal concentrations were significantly lower ( $p \le 0.05$ ) than for the WW treatment. In year 1, the Cu and Pb concentrations were greater ( $p \le 0.05$ ) for the WW and NP treatments than for the FW treatment. Comparatively, in year 2, the Cr and Pb concentrations were greater ( $p \le 0.05$ ) under WW than FW and NP. The FW and NP treatments had Fe root concentrations that were significantly different from each other, though neither were significantly different from WW. In year 1, the Pb concentration in the FW treatment was significantly different from the NP and WW treatments, though NP and WW treatments were not significantly different amongst themselves. The only significant difference in the concentration of Cu in potato roots in year 2 was between the FW and WW treatments.

Treatment	Metals							
	Cd	Cr	Cu	Fe	Pb	Zn		
	Year 1							
FW	1.92±0.94°	0.96±0.22°	8.90±2.31 <sup>b</sup>	$266.38 \pm 84.76^{b}$	$1.57 \pm 0.08^{b}$	41.42±15.05°		
WW	146.26±16.54 <sup>a</sup>	2.09±0.13 <sup>b</sup>	$39.54 \pm 8.80^{a}$	405.04±45.93 <sup>ab</sup>	27.12±3.02 <sup>a</sup>	217.36±26.80 <sup>a</sup>		
NP	64.71±25.43 <sup>b</sup>	$3.47 \pm 0.37^{a}$	$37.22 \pm 8.47^{a}$	$573.44 \pm 23.67^{a}$	$36.58 \pm 10.07^{a}$	114.66±23.6 <sup>b</sup>		
Year 2								
FW	2.79±0.72°	0.91±0.53 <sup>b</sup>	$22.24 \pm 5.84^{b}$	172.77±28.42 <sup>b</sup>	1.47±0.13 <sup>b</sup>	60.56±9.41°		
WW	249.69±43.02 <sup>a</sup>	2.79±0.90 <sup>a</sup>	72.35±36.61 <sup>a</sup>	1021.98±383.32 <sup>a</sup>	$38.74 \pm 18.16^{a}$	396.82±27.27 <sup>a</sup>		
NP	106.99±34.25 <sup>b</sup>	$1.27 \pm 0.09^{b}$	$31.15 \pm 12.87^{ab}$	417.79±88.27 <sup>b</sup>	14.15±2.22 <sup>b</sup>	177.49±25.57 <sup>b</sup>		

Table 6.4: Metal (Cd, Cr, Cu, Fe, Pb and Zn) concentrations in root in both years.

The values are the mean  $\pm$  standard error of 3 replicates; for each potato tissue category, different letters signify a significant difference ( $p \le 0.05$ ) column wise within tissue, year and metal contaminant.

#### 6.4.3.3 Aboveground Biomass (Stem & Leaves)

Metal's concentrations in the above ground biomass in both years are summarized in **Table 6.5**. Although the stem is not the edible, increased metal concentrations in the stem would suggest high transportation rates from below to above-ground biomass. The Cd concentration in potato stems was greater under WW than FW in year 1 and greater under NP than FW in year 2. The Cr and Cu concentrations in the potato stems were similar in all treatments across both years. A similar trend was also observed in Zn and Fe concentrations in year 1, and Pb concentration in year 2. While Fe and Zn concentrations were greater ( $p \le 0.05$ ) under WW than FW and NP in year 2, no significant differences were observed between FW and NP. A similar trend was observed for Fe and Zn in both years. The Pb root concentration in year 1 was greater ( $p \le 0.05$ ) under FW, though WW was not significantly different from either of these.

s	t	Metals							
Plant Part	Treatmen	Cd	Cr	Cu	Fe	Pb	Zn		
				Year 1					
ц	FW	1.71±1.15 <sup>b</sup>	$0.24\pm0.05^{a}$	$4.85 \pm 0.6^{a}$	40.28±19.61 <sup>a</sup>	1.12±0.27 <sup>b</sup>	41.74±21.27 <sup>a</sup>		
ten	WW	14.04±6.53ª	0.42±0.01ª	$7.62\pm2.67^{a}$	44.01±3.74 <sup>a</sup>	2.55±0.22 <sup>ab</sup>	37.95±7.81 <sup>a</sup>		
$\mathbf{N}$	NP	$8.27 \pm 4.07^{ab}$	$0.65 \pm 0.32^{a}$	$6.65 \pm 0.56^{a}$	49.10±19.44 <sup>a</sup>	$5.01 \pm 2.75^{a}$	55.46±38.11 <sup>a</sup>		
f	FW	0.97±0.51 <sup>b</sup>	$0.72\pm0.12^{a}$	7.04±1.17 <sup>b</sup>	201.20±36.60 <sup>a</sup>	2.20±0.47 <sup>b</sup>	10.65±1.62 <sup>a</sup>		
Lea	WW	$9.70 \pm 2.49^{a}$	2.66±1.24 <sup>a</sup>	$19.00 \pm 4.25^{a}$	306.97±115.31 <sup>a</sup>	$19.54 \pm 10.46^{a}$	13.97±2.81ª		
	NP	$7.36 \pm 4.37^{a}$	$1.61 \pm 1.32^{a}$	10.70±5.21 <sup>b</sup>	176.68±59.57 <sup>a</sup>	10.33±9.66 <sup>ab</sup>	$11.25 \pm 2.70^{a}$		
				Year 2					
eaf Stem	FW	2.87±2.11 <sup>b</sup>	0.32±0.14 <sup>a</sup>	6.64±3.44 <sup>a</sup>	32.74±9.01 <sup>b</sup>	1.03±0.70 <sup>a</sup>	49.06±13.40 <sup>b</sup>		
	WW	25.03±13.62 <sup>ab</sup>	$0.26\pm0.16^{a}$	12.88±6.35 <sup>a</sup>	69.18±24.82 <sup>a</sup>	$0.60\pm0.32^{a}$	93.64±4.38 <sup>a</sup>		
	NP	31.16±17.05 <sup>a</sup>	$0.34\pm0.30^{a}$	$8.89 \pm 3.56^{a}$	25.46±7.97 <sup>b</sup>	$0.69 \pm 0.54^{a}$	61.37±0.03 <sup>b</sup>		
	FW	5.41±4.83 <sup>b</sup>	0.30±0.13 <sup>a</sup>	9.78±0.81 <sup>b</sup>	145.64±26.36 <sup>a</sup>	$1.28\pm0.79^{a}$	10.72±1.13 <sup>b</sup>		
	WW	$15.35 \pm 1.30^{ab}$	$0.37 \pm 0.11^{a}$	22.21±6.74 <sup>a</sup>	231.93±54.16 <sup>a</sup>	2.16±0.01 <sup>a</sup>	$17.15 \pm 1.74^{a}$		
Π	NP	$15.81 \pm 5.38^{a}$	$1.10\pm0.72^{a}$	13.25±3.16 <sup>b</sup>	214.42±85.67 <sup>a</sup>	0.99±1.31ª	11.18±3.61 <sup>b</sup>		

Table 6.5: Metal (Cd, Cr, Cu, Fe, Pb and Zn) concentrations in Stem and Leaf in both years.

The values are the mean  $\pm$  standard error of 3 replicates; for each potato tissue category, different letters signify a significant difference ( $p \le 0.05$ ) column wise within tissue, year and metal contaminant.

In both years, for potato leaves, the NP treatment had greater ( $p \le 0.05$ ) Cd leaf concentrations than under FW but was not significantly different than under WW. No significant difference was observed for Cr and Fe leaf concentration between treatments in both years. Therefore, regardless of the treatment, Cr and Fe will accumulate in the potato leaves at the same level. A similar trend was also observed with respect to the Zn leaf concentration in year 1 and Pb in year 2. In year 1, Pb leaf concentrations were greater under WW than under FW, though neither were significantly different from NP. The WW treatment had significantly greater ( $p \le 0.05$ ) leaf concentrations of Cu than the other treatments in either year, while no significant differences were observed between FW and NP. A similar trend was observed for Zn leaf concentration in year 2.

## 6.5 Discussion

The purpose of this research was to investigate the impact of TiO<sub>2</sub>-NPs in wastewater on metal uptake by crops and mobility in the soil. The main significant findings were that TiO<sub>2</sub>-NPs in wastewater reduce the uptake of Cd, Cu and Zn by potato plants. While the literature has shown both positive and negative impacts of NPs on soil psychochemical properties (Hermes et al. 2020), in this study, TiO<sub>2</sub>-NPs, applied through wastewater, had no impact. Pachapur et al. (2016) found that TiO<sub>2</sub>-NPs are more mobile in mineral soils, like the sandy soil in this study, as compared to high organic colloid soil. This may have contributed to greater leaching of TiO<sub>2</sub>-NPs, which would explain why added TiO<sub>2</sub>-NPs was not detected in the soil and why there was no impact of soil physiochemical properties.

The presence of metals in the environment are considered a major source of soil contamination (Elbana et al., 2013; Talbot, 2007). Wastewater irrigation can add various metals in soil which are then likely to move through the soil profile (Fatta-Kassinos et al., 2011). Immobilization or stabilization of metal elements in the soil is a remediation process that involves reducing the mobility and bioavailability of pollutants through amendments, such as TiO<sub>2</sub>-NPs, that can absorb, minimize, complex or co-precipitate metals. It is possible that the TiO<sub>2</sub>-NPs absorb metals and increase their leaching, reducing plant uptake. For instance, Fang et al. (2011) found that soil NPs increased soil Cu transportation; however, the mechanism of Cu transportation was highly impacted by soil type.

A similar trend was observed for both Pb and Cu concentrations, which were greater than the permissible limits for agricultural soils (70 and 63 mg kg<sup>-1</sup>, respectively) (CCME, 2007). This implies that wastewater irrigation is a concern for Pb and Cu in topsoil. Overall, the Cr and Zn concentrations were within the CCME permissible limits for agricultural soil (64 and 250 mg kg<sup>-1</sup>, respectively). Our results suggested that a large amount of Cd, Cu and Pb are adsorbed on a narrow layer of surface soil. This study did not observe the effect of the presence NPs on metal mobility in the soil. Further experimentation is needed to understand how the presence of NPs in soil impacts metal mobility. Also, most studies using TiO<sub>2</sub>-NPs have been done in aqueous media, with only a few in soil.

In this study, the presence of  $TiO_2$ -NPs reduced the uptake of some metals to certain plant parts to the levels of the freshwater treatment (e.g leaf translocation in potatoes similar to the levels of the freshwater treatment). As such, our results provide important information about the potentials of  $TiO_2$ -NPs as an amendment to solve the problem of residual contamination in crop plants. Metal uptake and accumulation differed between plant tissues. Potato skins generally accumulated a greater concentration of heavy metals than did the flesh, likely because of its direct contact with the contaminated soil and irrigation water (Nzediegwu et al., 2019a).

While the exact mechanism requires further investigation, three main hypotheses emerge. Firstly, the TiO<sub>2</sub>-NPs may increase the immobilization of metals and reduce their bioavailability through co-precipitation, decreasing the metals in solution in the root zone. Secondly, through adsorption of metals, the TiO<sub>2</sub>-NPs may increase the mobility and leaching of metals in the soil, again reducing the amount available for uptake. Thirdly, TiO<sub>2</sub>-NPs could interact with the plant roots to indirectly decrease retention of metals in this area, thereby reducing uptake. For example, Rizwan et al. (2021) suggests that NPs can reduce the translocation of metals from roots to shoots by improving antioxidant defence systems, promoting structural changes, and changing gene expressions. Furthermore, Wu et al. (2021) found that TiO<sub>2</sub>-NPs decreased iron plaque on rice seedling roots which lead to a decrease in arsenic retention in this barrier and subsequently arsenic bioaccumulation. Many studies have reported that TiO<sub>2</sub>-NPs increase enzyme activities for enzymes that reduce oxidative stress, thereby increasing plant defence mechanisms (e.g., Ogunkunle et al., 2020a; Ogunkunle et al., 2020b). While this study found inconsistent impacts in Cd, Cu and Zn concentrations in above-ground biomass due to presence of TiO<sub>2</sub>-NPs, concentrations of these metals in below-ground biomass were reduced, suggesting that TiO<sub>2</sub>-NPs impacted both bioaccumulation through roots and metal translocation from roots to tubers. Furthermore, the size of TiO<sub>2</sub>-NPs likely has an important role in significant effects (Irshad et al., 2021), in comparison to granular/natural occurring TiO<sub>2</sub>-NPs in the soil. TiO<sub>2</sub>-NPs likely have a greater effect on metals in the soil-plant system than naturally occurring TiO<sub>2</sub> due to their physical properties (high surface area to volume ratio).

Despite the fact that TiO<sub>2</sub>-NPs are commonly used in food products and wastewater control, only a few studies have investigated their effects on metal toxicity and adsorption in the soil-plant systems (Qu et al., 2013; Youssef and Malhat, 2014). The immobilization of metal species from wastewater by NPs is complicated by the mixtures of contaminants found in wastewater. For example, metal speciation in solution is the result of competition between different metal complexes, chelates and free ions (Mahdavi et al., 2013). The sorption of metals by TiO<sub>2</sub>-NPs, is mainly controlled by adsorption between dissolved metals and hydroxyl groups at the particle surface (Koeppenkastrop and De Carlo, 1993). Previous studies indicated that NPs immobilize metals in soil solutions through reduction, physical sorption, chemical sorption and co-precipitation (Mahdavi et al., 2015b). NPs are characterized by having a high surface area and

high number of active sites, allowing for adsorption of metals (Mahdavi et al. (2015a); (Martínez-Fernández et al., 2015), thereby reducing their leachability and bioavailability, and therefore, transforming soluble and bioavailable metal fractions into stable residues (Liu and Zhao, 2007a, b; Mohamadiun et al., 2018).

Absorption of metals with NPs in soil and sediments is also possible. Cai et al. (2017) found that  $TiO_2$ -NPs at 1000 mg/L reduced Pb uptake in rice. Similarly, researchers (Cai et al., 2017; Yang and Zhang, 2009) have found that Pb ions were first attracted to the negatively charged surface sites of  $TiO_2$ -NPs through electrostatic interaction, while the surface hydroxyl groups coordinated with the Pb, which influenced the environmental fate and toxicity of this metal. However, it should be noted that  $TiO_2$ -NPs is negatively charged, while Pb and Cd are positively charged, which can impact on their complexation with NPs. Several studies have shown that the presence of metal- or carbon-based NPs can reduce the accumulation of metals in plants (Cai et al., 2017; Deng et al., 2017; Liu et al., 2017). Therefore, the interaction between soil minerals and NPs depends on the surface charge and the presence of soil minerals, which play an important role in sorption behaviour (Joo et al., 2009). The application of  $TiO_2$ -NPs enhanced bioaccumulation of Cd from polluted soils and reduced toxicity of Cd by increasing the photosynthesis rate (Singh and Lee, 2016).

Similarly, Nassar (2012) found that the surface charge of nano adsorbents can be either negative and acidic, attracting cations, or positive and basic, attracting anions. In the case of TiO<sub>2</sub>-NPs, particles are positively charged at pH<6 (Barakat, 2005). Since the soil pH was less than 6 in our study, it is assumed that TiO<sub>2</sub>-NPs were positively charged in the soil. While Nassar (2010 and 2012) found that adsorption was retarded at a lower pH, in the present study, cationic metals, like Cd, were better immobilized in an acidic soil environment. However, Pb is also

cationic and was not impacted by the presence of TiO<sub>2</sub>-NPs. Wang et al. (2015b) found that TiO<sub>2</sub>-NPs at pH 7.0 could strongly absorb Cu (II) and alleviation of phytotoxicity to rice seedling. In the present study, Cd and Zn uptake in potato tissues were reduced as a result of TiO<sub>2</sub>-NPs application. The reduction of Cd, induced by TiO<sub>2</sub>-NPs, is likely due to the reduction of free Cd<sup>2+</sup> by the hydroxyl group on the TiO<sub>2</sub>-NPs surface, which decreases Cd absorption in plant tissues (Mahdavi et al., 2013; Youssef and Malhat, 2014).

In agreement with our findings, Ji et al. (2017) found that  $TiO_2$ -NPs reduced Cd plant uptake and toxicity in rice. The authors suggested that the Cd adsorbed by  $TiO_2$ -NPs might possibly remain in solution, but become unavailable to the plants, thereby reducing Cd toxicity. Ji et al. (2017) reported that  $TiO_2$ -NPs adsorbed Cd more efficiently in nutrient solutions (similar to WW) than in fresh water. In general, adsorption onto metal (hydr)oxides is thought to occur via inner-sphere complexation with hydroxyls, making metal adsorption dependent on the adsorbing particle's specific surface area, density of active sites and pH of the point of zero charge (Wang et al., 2009). However, some metals may have a greater affinity to adsorption (*e.g.*, Cd), filling active sites hierarchically and preventing the adsorption of metals with lower affinities. Therefore, sorption competition may be the reason that  $TiO_2$ -NPs had no impact on Pb and Cr plant uptake, but did have an impact on Cd, Zn and Fe plant uptake.

Cadmium concentration in potato flesh in the present study was greater than the permissible limit of 0.1 mg kg<sup>-1</sup> (Codex, 1995), though under the presence of TiO<sub>2</sub>-NPs there was a lower Cd flesh concentration in Year 2, compared with the WW control. In year 2, Pb concentration in potato flesh was within the permissible limit of 0.1 mg kg<sup>-1</sup>, while in year 1 it was marginally above the permissible limit (Codex, 1995).

The effects on NPs on micronutrient uptake are inconsistent. Some studies have found that ZnO NPs increased Zn plant uptake (Liu et al., 2015; Munir et al., 2018), while others found that  $Fe_2O_3$  NPs decreased Fe plant uptake (Rui et al., 2018), suggesting that the impact of NPs on micronutrient uptake varies according to NPs, crop species, and environmental factors (Rizwan et al., 2019).

Bellani et al. (2020) found that the application of TiO<sub>2</sub>-NPs-spiked bio-solids to soil reduced the fraction of potentially available Fe, likely due to adsorption/complexation mechanisms. Their findings were consistent with our results, where Fe concentrations in the potato roots and flesh were lower under the presence of TiO<sub>2</sub>-NPs, compared with the WW control in Year 2. Similar reductions were also observed in the potato leaves over both years. It is likely that, TiO<sub>2</sub>-NPs adsorbed Fe in soil and reduced its bioavailability. This mechanism may also apply to other metals. Bellani et al. (2020) also found TiO<sub>2</sub>-NPs amendment resulted in a greater depletion of Zn in plant roots, though more work is needed to understand the mechanism. The present study also found that TiO<sub>2</sub>-NPs reduced the Zn in the roots in both years and stem and leaf in year 2 when compared to the WW control. It is possible that adsorption/complexation mechanisms also impact Zn.

The adsorption of certain metals can be enhanced by the specific functional groups of NPs (Li et al., 2011; Taghipour and Jalali, 2016; Wang et al., 2014). For example, TiO<sub>2</sub>-NPs have surface hydroxyl groups, which can impact the fate and toxicity of metals (Yang and Zhang, 2009).

The NPs may also induce a physiological response in plants. In petri dish studies with tobacco tissue, Frazier et al. (2014) found that  $TiO_2$ -NPs induced the expression of genes associated with plant oxidative stress, water transport, salt stress, and metal uptake. However, measuring  $TiO_2$ -NPs in plant tissues is challenging due to current methodological limitations,

namely the need to use a single particle ICP-MS, and challenges related to analysis in solids, rather than in solution. Iron oxide amendment reduced wheat seedling metal concentration, potentially due to the enhanced plant uptake of Zn and Fe in the presence of ZnO and Fe-NPs, which could compete with Cd at the surface of the roots (Konate et al., 2017). Both Bellani et al., (2020) and López-Luna et al. (2016) found that metal oxide nanoparticles reduced Cd toxicity to plants by decreasing Cd and other metals' mobility, bioavailability and bio-accessibility. Ogunkunle et al. (2020b) found that the application of  $TiO_2$  NPs significantly reduced (32%) the Cd uptake by cowpea Plants. The authors noted that  $TiO_2$  NPs are known to possess strong potential to adsorb toxic metals on their surfaces, thereby rendering Cd ions unavailable for uptake through roots. Similar observations were reported by Kuang et al. (2020) who found that TiO<sub>2</sub>-NPs enhanced the removal of Cd by biological soil crusts under acidic irrigation water. Investigating the mechanism that led to a reduction in Cd uptake and bioaccumulation in cowpea tissues by foliar-applied  $nTiO_2$ , it appeared that foliar application of nTiO<sub>2</sub> only reduced but did not stop Cd translocation to aboveground biomass (Ogunkunle et al., 2020a). Nonetheless, the evidence that TiO<sub>2</sub>-NPs can alleviate the toxicity of Cd in rice, and in potatoes, suggest that  $TiO_2$ -NPs may provide a new solution to metal contamination in crop plants.

Overall, the presence of TiO<sub>2</sub>-NPs in WW can reduce crop uptake of metals in WW irrigation, lowering risks associated with wastewater irrigation. After all, soils are one of the most important sinks for pollutants in the environment. Furthermore, TiO<sub>2</sub>-NPs may be a viable amendment for growing crops on contaminated soil. As the use of TiO<sub>2</sub>-NPs in agricultural applications is increasing, such as through fertilizers or herbicides, this research suggests that application will not increase plant uptake of metals if they are present in soil or irrigation water and may have the positive impact of decreasing the uptake of Cd, Cu and Zn. Moreover, further

study of NP size effects on plant growth is important as well (Clément et al., 2013; Georgantzopoulou et al., 2012), as different sizes of NPs could lead to different types of phytotoxicity. The related work on how to safely use NPs to lower the toxicity of metals in agriculture through long-term field experiments is currently underway. This study recommends further research to understand the mechanism of how TiO<sub>2</sub>-NPs interact with metals, soils particles and plants to reduce the uptake of metals by plants.

## 6.6 Conclusions

Both metals and metal-based nanoparticles (NPs) are common pollutants, although little is known about their potential co-contaminant interactions, including impacts on sensitive biota such as food crops. Research on co-exposure to metals and metal-based NPs is limited, and plant responses in terms of physiological parameters, contaminant accumulation, and defense mechanisms are poorly understood. In the present two years of study, potato plants were co-exposed to six metals and titanium oxide nanoparticles (TiO<sub>2</sub>-NPs). The latter significantly reduced the uptake of Cd, Cu and Zn into potato in terms of belowground biomass (roots and tubers).

Over this two-year experiment, there were no effects of the concentration of  $TiO_2$ -NPs in the wastewater on the soil physicochemical properties and soil metal mobility. The influence of TiO\_2-NPs on the plant uptake of metals in potato tissues was investigated. It appears that TiO\_2-NPs activated protective mechanisms that reduced metals' uptake by a root crop such as potatoes. Furthermore, the alleviating effect of TiO\_2-NPs is associated with their adsorption capacity towards metals and competition with metals, which could be due to different co-contaminants' interactions, *e.g.*, between TiO\_2-NPs and metal cations.

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# **Chapter 7. General summary and conclusions**

The reuse of untreated wastewater for irrigating crops appears to be an alternative technique with potential to alleviate pressure on limited freshwater resources, particularly in arid and semi-arid areas. Wastewater irrigation can, however, be one of the main reasons for contaminant accumulation in crops. Depending on the concentration of pollutants in the wastewater, various consequences could occur, such as health threats to humans and the environment. For example, in some severely polluted areas, plants could accumulate high concentrations of contaminants that might exceed acceptable limits for human consumption. The main objective of the thesis was to develop an economically feasible remediation technique to reduce the bioavailability of heavy metals and emerging organic contaminants caused by wastewater irrigation of agricultural crops. A lysimeter study was undertaken to determine the influence of barley straw biochar and green and table waste compost soil amendments, alone or in combination, along with wastewater-borne amendments of TiO<sub>2</sub>-NPs, on heavy metal and emerging organic contaminants' fate and transport. The impact of wastewater irrigation on potato production and the effects of the amendments on crop growth were also investigated. Given these objectives, the following conclusions were drawn from the current study:

The first study was conducted to determine the effects of soil amendments, such as barley straw biochar and green and table waste compost, on heavy metal uptake by potatoes and their soil transport with wastewater irrigation. The study found that compost alone or mixed with biochar was effective in reducing potato plant uptake of Cd, Cu and Zn and retained the metals in the topsoil. Tuber peel and root parts accumulated more heavy metals than potato flesh because of their direct contact with soil, while different heavy metals showed different trends of uptake and translocation in potato plants. We attributed the compost's effect on its ability to change soil physiological parameters such as CEC, DOC, and pH.

The effects of the soil amendments on potato plant growth and yield were also investigated. Biochar and biochar-compost amendments improved potato growth under wastewater irrigation, in comparison to the wastewater control. Biochar application rates and biochar: compost mixing ratios significantly ( $p \le 0.05$ ) improved soil physicochemical properties (*e.g.*, cation exchange capacity, soil organic matter, and pH) and potato yield.

Another part of this study examined the effects of the soil amendments on soil transport of PPCPs in wastewater in a sandy soil. Biochar proved to be more effective than compost in retaining three PPCPs, namely CAF, CBZ and DEET, in topsoil. This effect was attributed to the interaction of PPCPs with biochar's surface functional groups, confirmed through FTIR analysis, and the modulation of soil and PPCPs' physicochemical properties These were all key to determining the fate of PPCPs in the soil profile.

Another study was conducted to determine the effects of TiO<sub>2</sub>-NPs on the mobility and heavy metal uptake by potato plants. The presence of TiO<sub>2</sub>-NPs in wastewater had no effect on heavy metal concentrations in the soil profile; there being no significant ( $p \le 0.05$ ) difference between treatments (WW vs. WW+NP), indicating an even distribution of heavy metals in the upper soil matrix. Potato peels and roots accumulated more heavy metals than the tuber flesh because of their direct contact with soil. Different heavy metals showed different trends of uptake and translocation in plants. TiO<sub>2</sub>-NPs was able to reduce the concentration of Cd, Cu and Zn in below-ground biomass tissue. We attributed these effects on the ability of TiO<sub>2</sub>-NPs to increase the activity of enzymes that reduce oxidative stress, thereby increasing plant defense mechanisms. Overall, this thesis indicates that sorptive soil amendments and the presence of NPs in wastewater could contribute to the safe use of wastewater in irrigation by reducing plant uptake of certain heavy metals and decreasing organic contaminates mobility. Sorptive materials, biochar and compost, were found to reduce bioavailability of contaminants by improving soil physiochemical properties that facilitate immobilization. Furthermore, the wastewater can be a sustainable source of irrigation water in freshwater-scarce countries. Future research is needed to determine the mechanisms behind the effectiveness of nanoparticles in wastewater on reducing plant uptake of containments.

# **Chapter 8. Contributions to knowledge and suggestions for future research**

### **Contributions to Knowledge**

This study looked into the effect of two eco-friendly and cost-effective soil amendments on the dynamics of coexisting organic and inorganic pollutants in soil under wastewater irrigation. This work can lead to the development of easy-to-use new technologies for using large volumes of partially treated or untreated wastewaters in agriculture.

The following are the major contributions to knowledge from this work:

1. This study is the first of its kind to investigate the effect of two rates of biochar application, alone or mixed, with compost as a soil amendment on the fate and transport of several coexisting emerging organic contaminants (*e.g.*, pharmaceuticals and personal care products), in a soil-plant system under wastewater irrigation. This study has revealed that higher biochar application rates may immobilizes PPCPs in soil.

2. For the first time, the effectiveness of different application rates of barley straw biochar, alone or in combination with compost, has been assessed for heavy metal fate and transport under wastewater irrigation.

3. To the author's knowledge, this study, for the first time, investigated the impact of  $TiO_2$  NPs in wastewater on the fate of heavy metals in soil under wastewater irrigation. This study has revealed that  $TiO_2$  NPs in wastewater have a significant impact on heavy metal uptake by potatoes.

#### **Recommendations for Future Works**

Suggestions and recommendations for future research are given as follows:

1. The use of partially treated or treated effluents for irrigation is an agricultural land management strategy that can have many potential benefits. However, in order to assess the feasibility of wastewater irrigation, long-term field studies must investigate how this impacts the long-term chemical, biochemical and microbiological characteristics of soil, along with plant growth and plant accumulation of inorganic and organic pollutants.

2. There remains substantial gaps in our understanding of the environmental impact, fate, and behavior of pharmaceuticals and personal care products, thus limiting our ability to predict the human and environmental health effects of the application of untreated or partially treated wastewater to agricultural land. One major barrier is the lack of mechanistic information on plant translocation and distribution of PPCPs.

3. Further studies on the mechanism of  $TiO_2$ -NPs and metals interactions in soil-plant system are required. The plant physiological reaction to the presence of NPs should also be investigated. Research could also investigate the impact, fate and transport of other NPs in wastewater.

4. Competitive sorption-desorption properties of various pollutants (mono and multiinorganic) to biochar and/or compost through sorption and desorption tests should be studied. These experiments could predict the synergetic and antagonistic relationships between different heavy metals that could potentially affect their mobility and bioavailability.

5. Similar experiments may also be undertaken on other soil types and for various other crops to determine the effectiveness of soil amendments and establish guidelines, depending on the

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type of soil and crop under variations in environmental conditions and different levels of water stress.

6. In this study, biochar and compost use was limited to only one type of biochar, one type of compost, and one type of soil. Similar experiments may be conducted in other soil types, using different types of biochar and compost, obtained from different feedstocks.

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## Appendix

stomatal conductance of potato plants in 2018.								
	Day-45	Day-55	Day-65	Day-75	Day-85	Day-95		
Photosynthesis Rate (µmol CO <sub>2</sub> m <sup>-2</sup> s <sup>-1</sup> )								
FW	9.62±1.38 <sup>ab</sup>	10.43±4.02ª	$10.12 \pm 2.07^{a}$	8.36±1.24 <sup>a</sup>	$4.77 \pm 2.76^{b}$	5.39±1.92ª		
WW	12.46±1.53 <sup>a</sup>	13.20±1.05ª	$10.82 \pm 1.06^{a}$	8.36±4.16 <sup>a</sup>	$10.05 \pm 1.85^{a}$	4.81±1.21 <sup>ab</sup>		
FW+NP	8.58±1.1 <sup>b</sup>	9.88±0.91ª	9.79±3.1ª	$7.62{\pm}1.57^{a}$	$5.55 {\pm} 1.87^{b}$	1.58±2.13 <sup>b</sup>		
WW+NP	$10.75 \pm 2.52^{ab}$	11.96±1.65ª	12.44±3.07ª	7.98±0.88ª	$9.64 \pm 0.4^{a}$	5.43±0.31ª		
<b>Transpiration Rate</b> (mmol H <sub>2</sub> O m <sup>-2</sup> s <sup>-1</sup> )								
FW	$0.65 \pm 0.18^{ab}$	$3.11 \pm 1.67^{a}$	$3.27{\pm}0.56^{ab}$	2.62±1.11ª	$0.95 \pm 0.56^{a}$	2±0.55ª		
WW	0.88±0.33ª	$4.32 \pm 1.04^{a}$	3.62±0.37 <sup>ab</sup>	2.28±1.94ª	1.49±0.11 <sup>a</sup>	1.01±0.37 <sup>ab</sup>		
FW+NP	$0.31 \pm 0.07^{b}$	$3.69 \pm 0.47^{a}$	$2.70 \pm 0.60^{b}$	1.96±0.48 <sup>a</sup>	$1.08 \pm 0.51^{a}$	0.84±0.71 <sup>b</sup>		
WW+NP	0.61±0.19 <sup>ab</sup>	$3.34\pm0.97^{a}$	3.79±0.69ª	1.58±0.37 <sup>a</sup>	1.32±0.27ª	1.46±0.05 <sup>ab</sup>		
Stomatal Conductance (mol H <sub>2</sub> O m <sup>-2</sup> s <sup>-1</sup> )								
FW	$0.08 \pm 0.02^{ab}$	$0.27 \pm 0.26^{a}$	$0.37{\pm}0.14^{a}$	0.21±0.15 <sup>a</sup>	0.12±0.08ª	0.12±0.06 <sup>a</sup>		
WW	0.12±0.05ª	$0.36 \pm 0.17^{a}$	$0.42 \pm 0.07^{a}$	0.18±0.19 <sup>a</sup>	0.20±0.02 <sup>a</sup>	$0.05 \pm 0.02^{ab}$		
FW+NP	$0.04 \pm 0.01^{b}$	0.23±0.04ª	$0.28{\pm}0.08^{a}$	0.12±0.03ª	0.13±0.07ª	0.04±0.03 <sup>b</sup>		
WW+NP	0.08±0.03 <sup>ab</sup>	0.21±0.09ª	0.44±0.13ª	0.10±0.03ª	$0.17 \pm 0.04^{a}$	$0.07 \pm 0.01^{ab}$		

Appendix 1: Effect of freshwater (FW), wastewater (WW), freshwater with TiO<sub>2</sub>-NPs (FW+NP), and wastewater with TiO<sub>2</sub>-NPs (WW+NP), on photosynthetic rate, transpiration rate and stomatal conductance of potato plants in 2018.

Treatments	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )		SOM (%)		рН	
	Surface	0.10 m	Surface	0.10 m	Surface	0.10 m
FW	3.14±0.50 <sup>a</sup>	3.19±0.33ª	1.74±0.05 <sup>b</sup>	1.74±0.05 <sup>b</sup>	5.76±0.11ª	5.70±0.20 <sup>a</sup>
WW	1.79±0.29°	2.62±1.24 <sup>a</sup>	2.80±0.64 <sup>a</sup>	2.72±0.19 <sup>a</sup>	$5.00 \pm 0.10^{b}$	5.26±0.15 <sup>a</sup>
FW+NP	2.85±0.30 <sup>ab</sup>	2.77±0.10 <sup>a</sup>	1.79±0.11 <sup>b</sup>	1.79±0.11 <sup>b</sup>	5.76±0.11ª	5.76±0.11ª
WW+NP	2.33±0.31 <sup>bc</sup>	3.44±1.81 <sup>a</sup>	2.60±0.55ª	2.69±0.06 <sup>a</sup>	$5.08 \pm 0.07^{b}$	5.30±0.30 <sup>a</sup>

Appendix 2: Effects of freshwater (FW), wastewater (WW), freshwater with TiO<sub>2</sub>-NPs (FW+NP), and wastewater with TiO<sub>2</sub>-NPs (WW+NP), on soil cation exchange capacity (CEC), soil organic matter (SOM), and pH.

	Day-55	Day-65	Day-75	Day-85	Day-95
2017					
FW	$0.85 \pm 0.05^{a}$	$0.84{\pm}0.01^{a}$	$0.76 \pm 0.05^{a}$	$0.67 \pm 0.09^{a}$	$0.62 \pm 0.16^{b}$
WW	$0.88 \pm 0.02^{a}$	$0.80\pm0.12^{a}$	0.76±0.10 <sup>a</sup>	$0.65 \pm 0.15^{a}$	$0.75 \pm 0.10^{ab}$
FW+NP	$0.68\pm0.14^{b}$	$0.76 \pm 0.16^{a}$	$0.82 \pm 0.04^{a}$	$0.84\pm0.02^{a}$	$0.84\pm0.07^{a}$
WW+NP	0.86±0.04ª	$0.79 \pm 0.08^{a}$	$0.82 \pm 0.04^{a}$	$0.78\pm0.18^{a}$	$0.82\pm0.08^{ab}$
2018					
FW	0.79±0.05ª	$0.82 \pm 0.03^{a}$	$0.85{\pm}0.02^{ab}$	$0.78 \pm 0.03^{a}$	0.83±0.03ª
WW	$0.77 \pm 0.02^{a}$	$0.79{\pm}0.14^{a}$	$0.85 \pm 0.02^{a}$	$0.79 \pm 0.05^{a}$	$0.82\pm0.05^{a}$
FW+NP	0.75±0.11ª	$0.80 \pm 0.09^{a}$	$0.79 \pm 0.03^{b}$	0.74±0.11ª	0.84±0.01ª
WW+NP	$0.80{\pm}0.06^{a}$	$0.73 \pm 0.22^{a}$	$0.74 \pm 0.04^{\circ}$	$0.81 \pm 0.08^{a}$	0.79±0.14 <sup>a</sup>

Appendix 3: Effect of freshwater (FW), wastewater (WW), freshwater with  $TiO_2$ -NPs (FW+NP), and wastewater with  $TiO_2$ -NPs (WW+NP), on normalized difference vegetation index (NDVI) readings on potato plants in 2017 and 2018.

	Tuber Weight (kg)		No. of Tubers		% Tuber grading (>50mm)	
	2017	2018	2017	2018	2017	2018
FW	0.86±0.06 <sup>a</sup>	0.58±0.20 <sup>a</sup>	17.33±4.51 <sup>a</sup>	6.66±3.05 <sup>a</sup>	19.61±13.54ª	48.33±44.81ª
WW	0.89±0.11 <sup>a</sup>	0.64±0.30 <sup>a</sup>	15.33±3.51 <sup>a</sup>	6.66±2.31 <sup>a</sup>	39.88±17.77 <sup>a</sup>	54.16±7.21 <sup>a</sup>
FW+NP	$0.32 \pm 0.06^{b}$	0.35±0.16 <sup>a</sup>	$7.33 {\pm} 2.88^{b}$	6.33±1.15 <sup>a</sup>	43.52±27.82ª	47.62±45.92ª
WW+NP	$0.77 \pm 0.38^{a}$	0.64±0.11 <sup>a</sup>	10.66±6.43 <sup>ab</sup>	$7.66 \pm 3.05^{a}$	38.89±9.62ª	40.34±21.02 <sup>a</sup>

Appendix 4: Effect of freshwater (FW), wastewater (WW), freshwater with  $TiO_2$ -NPs (FW+NP), and wastewater with  $TiO_2$ -NPs (WW+NP), on potato tuber weight, number of tubers, and tuber grading in 2017 and 2018.

Treatment	C-Flesh	C-Leaf	N-Flesh	N-Leaf
2017				
FW	$40.23\pm0.22^{a}$	$41.13 \pm 0.28^{ab}$	$1.04 \pm 0.27^{\circ}$	$2.60 \pm 0.56^{b}$
FW+NP	$39.98 \pm 0.95^{a}$	$42.21 \pm 1.01^{a}$	$1.65 \pm 0.07^{ab}$	$3.96 \pm 0.13^{a}$
WW	$40.84 \pm 0.17^{a}$	$39.96 \pm 1.52^{b}$	$1.47 \pm 0.08^{bc}$	$4.01 \pm 0.28^{a}$
WW+NP	$40.90 \pm 0.95^{a}$	$41.75 \pm 0.45^{ab}$	$1.99 \pm 0.46^{a}$	$4.04 \pm 0.38^{a}$
2018				
FW	$40.24 \pm 0.21^{a}$	$43.80 \pm 0.47^{a}$	$1.50 \pm 0.18^{b}$	$3.54 \pm 0.51^{b}$
FW+NP	$40.28 \pm 0.07^{a}$	$43.89 \pm 0.33^{a}$	1.63 ±0.09 <sup>ab</sup>	$4.60 \pm 0.84^{ab}$
WW	$40.46 \pm 0.34^{a}$	$42.96 \pm 0.44^{ab}$	$1.57 \pm 0.18^{ab}$	$4.48 \pm 0.92^{ab}$
WW+NP	$40.55 \pm 0.19^{a}$	$42.75 \pm 0.79^{b}$	$1.82 \pm 0.20^{a}$	$4.84 \pm 0.28^{a}$

Appendix 5: Effect of freshwater (FW), wastewater (WW), freshwater with  $TiO_2$ -NPs (FW+NP), and wastewater with  $TiO_2$ -NPs (WW+NP), on total content of carbon and nitrogen in potato flesh and leaf in 2017 and 2018.



Appendix 6: Effect of freshwater (FW), wastewater (WW), freshwater with TiO<sub>2</sub>-NPs (FW+NP) and wastewater with TiO<sub>2</sub>-NPs (WW+NP) irrigation on potato plant greenness in 2017 and 2018. The different letters on the bars in each column represent significant difference at  $p \le 0.05$  (Mean  $\pm$  SD, n = 3).





Year



Appendix 7: Effects of freshwater (FW), wastewater (WW), freshwater with TiO<sub>2</sub>-NPs (FW+NP), and wastewater with TiO<sub>2</sub>-NPs (WW+NP), on potato plant height, root weight, and shoot weight in 2017 and 2018. The different letters on the bars in each column represent significant difference at  $p \le 0.05$  (Mean ± SD, n = 3).



Appendix 8: Measured CO<sub>2</sub> flux of all treatments in 2017, the different letters on the bars in each column represent significant difference at  $p \le 0.05$  (Mean ± SD, n = 3).



Appendix 9: Measured CO<sub>2</sub> flux of all treatments in 2018, the different letters on the bars in each column represent significant difference at  $p \le 0.05$  (Mean ± SD, n = 3).